A Mathematical Model of Daisy Chain Aggregation

In order to appreciate the dramatic effects concentration can play in the assembly of these daisy chain superstructures, an Excel spreadsheet was written (see below) in order to plot concentration profiles for daisy chain assemblies (up to, and including, trimers), based upon assumed values of K_a for the appropriate equilibria. Also, at this juncture, a shorthand method for annotating different daisy chain species is introduced: *a* denotes acyclic, whereas *c* denotes cyclic; and, in each case, the numerical suffix refers to the value of DP, *i.e.*, a dimer is 2, a trimer is 3, *etc.* The model employed (Figure S1) for these calculations assumes[1] that no oligomers larger than trimers are formed, thus limiting the resulting algorithm to a cubic equation (rather than a potentially insoluble quartic—or even higher order—equation). The expressions for equilibrium (K_a) values (Equations 1–5) are simply rearranged (with appropriate substitution of terms) to give expressions (Equations 6–10) for the concentration of each aggregated daisy chain species in terms of [*a*1]. The total dissolved monomer concentration ([*M*]) is given simply by Equation 11, into which the results of Equations 6–10 can be substituted to give an expression (Equation 12), which is subsequently rearranged to give a cubic equation (Equation 13) which can be solved for [*a*1]. Subsequently, this value of [*a*1] can be substituted back into Equations 6–10, to give the concentrations of each of the aggregated daisy chain species. By assuming reasonable K_a values for each equilibrium process shown in Figure S1, it is then possible to plot how the percentage concentration of any given species in solution varies (Figure S2) depending upon how much daisy chain monomer (*M*) is initially dissolved. Initially (Figure S2i), K_{a2} was assumed to be 320 M^{-1} (the same K_a value[2] as that obtained in CD_3CN for the threading of the dibenzylammonium cation through DB24C8), and K_{a3} was given a slightly lower value of 210 M^{-1}. The K_a values for cyclization (K_{c1}, K_{c2}, and K_{c3}), were chosen as 0, 640, and 480, respectively, reflecting the fact that intramolecular self-complexation is not possible, but that dimerization is further favored by the π–π stacking of the central aromatic rings of **1**-H^+, and that there may also be a degree of cooperativity in cyclic trimerization. Given these values, it can be seen (Figure S2i) that, over a wide concentration range (10^{-4}–10 M), the cyclic dimeric daisy chain ([*c*2]) predominates in solution. Based upon the dilution studies described in this Paper, however, it has been observed that, at 0.026 mM, only daisy chain monomer is observed in CD_3CN solution. To fit this observed data, the estimates of K_a values were reduced[3] (Figure S2ii) to give a new concentration profile. Using these values, a plot is obtained which still shows that cyclic dimer dominates in solution from 10^{-3}–10 M, but at significantly lower concentration, *i.e.*, 0.026 mmol, the daisy chain monomer is now the most abundant species. Therefore, although only an approximation, this spreadsheet can be used—in conjunction with experimental data—to estimate the equilibrium values for cyclization/oligomerization in such self-complementary aggregating systems.

The [25]crown-8 system

Using the K_a values determined for the self-aggregation of **29**-H·PF_6 at 71.4 mM, the concentration profile of this system can be plotted (Figure S3) using this spreadsheet. This plot not only reveals that significant amounts of [*a*3]- and [*c*3]daisy chain are only expected to form at relatively high monomer concentrations (> 1 M), but it also serves to confirm the ^{19}F NMR spectroscopic observations made on 2.0 and 12.7 mM solutions of **29**-H·PF_6, respectively. The ^{19}F NMR spectrum, obtained from the 12.7 mM solution, contained peaks (recall Figure 16) corresponding to the presence of [*a*1]-, [*a*2]-, and [*c*2]daisy chains with percentage concentrations of 87.8, 5.6, and 6.6, respectively. The percentage concentrations of these species, as predicted from the concentration profile shown in Figure S3, are 85.0, 6.5, and 7.8, respectively, values which are within experimental error of those observed experimentally. Furthermore, the [*a*3]- and [*c*3]daisy chains are predicted to account for 0.4 and 0.3 %, respectively, of the total concentration of all species in solution, a result that explains why signals for these species are not observed in the 12.7 mM spectrum. When considering the most dilute solution (2.0 mM), only one signal—arising from the [*a*1] monomer—is observed. Once again, this result can be rationalized by using the concentration profile plotted in Figure S3. It predicts that ~97 % of the 2.0 mM solution is anticipated to be the monomeric species, with only ~1.5 % of both [*a*2]- and [*c*2]daisy chains being present. Unless it is a remarkable coincidence, the good agreement between theory and experiment is surely a testament to both (i) the assignment of peaks in the concentration-dependent ^{19}F NMR spectra of **29**-H·PF_6 and (ii) the validity of the model employed in the construction of the concentration profiles.

The plots obtained above were obtained using a spreadsheet written in Microsoft Excel 98. The spreadsheet has the capacity to solve both reducible and irreducible cubic equations, and follows standard methods, as discussed in Rosenbach, J. B.; Whitman, E. A. *College Algebra, (Revised Edition)*; Ginn and Company: Boston, 1939, pp. 265–269. What follows are the cell entries: those containing *comments* are italicized, those requiring **input** are in bold, and those containing calculations and/or equalities appear in regular text.

A1 = *"Total Dissolved Monomer Concentration [M] in M"*
B1 = *"Log_{10}[M]"*
C1 = *"K_{a2} (M^{-1})"*
D1 = *"[a1] (M)"*
E1 = *"[a2] (M)"*
F1 = *"[a3] (M)"*
G1 = *"[c1] (M)"*
H1 = *"[c2] (M)"*
I1 = *"[c3] (M)"*
J1 = *"Total Concentration of Species in Solution"*
K1 = *"Total Dissolved Monomer Concentration [M] in M"*

L1	=	*"%a1"*
M1	=	*"%c1"*
N1	=	*"%a2"*
O1	=	*"%c2"*
P1	=	*"%a3"*
Q1	=	*"%c3"*
R1	=	*"100%"*
A2	=	0.000001
B2	=	LOG(A2)
C2		**Enter value of K_{a2} (M^{-1}) in here**
D2	=	F51
E2	=	C2*(F51^2)
F2	=	C2*C4*(F51^3)
G2	=	C6*F51
H2	=	C8*C2*(F51^2)
I2	=	C10*C4*C2*(F51^3)
J2	=	I2+H2+G2+F2+E2+D2
K2	=	(F51*(1+C6))+((F51^2)*((2*C2)+(2*C2*C8)))+((F51^3)*(3*C2*C4)+(3*C10*C4*C2)))
L2	=	(D2/J2)*100
M2	=	(G2/J2)*100
N2	=	(E2/J2)*100
O2	=	(H2/J2)*100
P2	=	(F2/J2)*100
Q2	=	(I2/J2)*100
R2	=	L2+M2+N2+O2+P2+Q2
A3	=	0.00001
B3	=	LOG(A3)
C3	=	*"K_{a3} (M^{-1})"*
D3	=	F87
E3	=	C2*(F87^2)
F3	=	C2*C4*(F87^3)
G3	=	C6*F87
H3	=	C8*C2*(F87^2)
I3	=	C10*C4*C2*(F87^3)
J3	=	I3+H3+G3+F3+E3+D3
K3	=	(F87*(1+C6))+((F87^2)*((2*C2)+(2*C2*C8)))+((F87^3)*(3*C2*C4)+(3*C10*C4*C2)))
L3	=	(D3/J3)*100
M3	=	(G3/J3)*100
N3	=	(E3/J3)*100
O3	=	(H3/J3)*100
P3	=	(F3/J3)*100
Q3	=	(I3/J3)*100
R3	=	L3+M3+N3+O3+P3+Q3
A4	=	0.0001
B4	=	LOG(A4)
C4		**Enter value of K_{a3} (M^{-1}) in here**
D4	=	F124
E4	=	C2*(F124^2)
F4	=	C2*C4*(F124^3)
G4	=	C6*F124
H4	=	C8*C2*(F124^2)
I4	=	C10*C4*C2*(F124^3)
J4	=	I4+H4+G4+F4+E4+D4
K4	=	(F124*(1+C6))+((F124^2)*((2*C2)+(2*C2*C8)))+((F124^3)*(3*C2*C4)+(3*C10*C4*C2)))
L4	=	(D4/J4)*100
M4	=	(G4/J4)*100
N4	=	(E4/J4)*100
O4	=	(H4/J4)*100
P4	=	(F4/J4)*100
Q4	=	(I4/J4)*100
R4	=	L4+M4+N4+O4+P4+Q4
A5	=	0.001
B5	=	LOG(A5)
C5	=	*"K_{c1}"*
D5	=	F161

E5 = C2*(F161^2)
F5 = C2*C4*(F161^3)
G5 = C6*F161
H5 = C8*C2*(F161^2)
I5 = C10*C4*C2*(F161^3)
J5 = I5+H5+G5+F5+E5+D5
K5 = (F161*(1+C6))+((F161^2)*((2*C2)+(2*C2*C8)))+((F161^3)*(3*C2*C4)+(3*C10*C4*C2)))
L5 = (D5/J5)*100
M5 = (G5/J5)*100
N5 = (E5/J5)*100
O5 = (H5/J5)*100
P5 = (F5/J5)*100
Q5 = (I5/J5)*100
R5 = L5+M5+N5+O5+P5+Q5
A6 = 0.01
B6 = LOG(A6)
C6 **Enter value of K_{c1} (pure number) in here**
D6 = F197
E6 = C2*(F197^2)
F6 = C2*C4*(F197^3)
G6 = C6*F197
H6 = C8*C2*(F197^2)
I6 = C10*C4*C2*(F197^3)
J6 = I6+H6+G6+F6+E6+D6
K6 = (F197*(1+C6))+((F197^2)*((2*C2)+(2*C2*C8)))+((F197^3)*(3*C2*C4)+(3*C10*C4*C2)))
L6 = (D6/J6)*100
M6 = (G6/J6)*100
N6 = (E6/J6)*100
O6 = (H6/J6)*100
P6 = (F6/J6)*100
Q6 = (I6/J6)*100
R6 = L6+M6+N6+O6+P6+Q6
A7 = 0.1
B7 = LOG(A7)
C7 = *"K_{c2}"*
D7 = F234
E7 = C2*(F234^2)
F7 = C2*C4*(F234^3)
G7 = C6*F234
H7 = C8*C2*(F234^2)
I7 = C10*C4*C2*(F234^3)
J7 = I7+H7+G7+F7+E7+D7
K7 = (F234*(1+C6))+((F234^2)*((2*C2)+(2*C2*C8)))+((F234^3)*(3*C2*C4)+(3*C10*C4*C2)))
L7 = (D7/J7)*100
M7 = (G7/J7)*100
N7 = (E7/J7)*100
O7 = (H7/J7)*100
P7 = (F7/J7)*100
Q7 = (I7/J7)*100
R7 = L7+M7+N7+O7+P7+Q7
A8 = 1
B8 = LOG(A8)
C8 **Enter value of K_{c2} (pure number) in here**
D8 = F271
E8 = C2*(F271^2)
F8 = C2*C4*(F271^3)
G8 = C6*F271
H8 = C8*C2*(F271^2)
I8 = C10*C4*C2*(F271^3)
J8 = I8+H8+G8+F8+E8+D8
K8 = (F271*(1+C6))+((F271^2)*((2*C2)+(2*C2*C8)))+((F271^3)*(3*C2*C4)+(3*C10*C4*C2)))
L8 = (D8/J8)*100
M8 = (G8/J8)*100
N8 = (E8/J8)*100
O8 = (H8/J8)*100

P8 = (F8/J8)*100
Q8 = (I8/J8)*100
R8 = L8+M8+N8+O8+P8+Q8
A9 = 10
B9 = LOG(A9)
C9 = *"K_{c3}"*
D9 = F309
E9 = C2*(F309^2)
F9 = C2*C4*(F309^3)
G9 = C6*F309
H9 = C8*C2*(F309^2)
I9 = C10*C4*C2*(F309^3)
J9 = I9+H9+G9+F9+E9+D9
K9 = (F309*(1+C6))+((F309^2)*((2*C2)+(2*C2*C8)))+((F309^3)*(3*C2*C4)+(3*C10*C4*C2)))
L9 = (D9/J9)*100
M9 = (G9/J9)*100
N9 = (E9/J9)*100
O9 = (H9/J9)*100
P9 = (F9/J9)*100
Q9 = (I9/J9)*100
R9 = L9+M9+N9+O9+P9+Q9
A10 = 100
B10 = LOG(A10)
C10 **Enter value of K_{c3} (pure number) in here**
D10 = F346
E10 = C2*(F346^2)
F10 = C2*C4*(F346^3)
G10 = C6*F346
H10 = C8*C2*(F346^2)
I10 = C10*C4*C2*(F346^3)
J10 = I10+H10+G10+F10+E10+D10
K10 = (F346*(1+C6))+((F346^2)*((2*C2)+(2*C2*C8)))+((F346^3)*(3*C2*C4)+(3*C10*C4*C2)))
L10 = (D10/J10)*100
M10 = (G10/J10)*100
N10 = (E10/J10)*100
O10 = (H10/J10)*100
P10 = (F10/J10)*100
Q10 = (I10/J10)*100
R10 = L10+M10+N10+O10+P10+Q10
A11 **Enter a specific value of [*M*] (M) in here to determine the resulting solution composition**
B11 = LOG(A11)
D11 = F382
E11 = C2*(F382^2)
F11 = C2*C4*(F382^3)
G11 = C6*F382
H11 = C8*C2*(F382^2)
I11 = C10*C4*C2*(F382^3)
J11 = I11+H11+G11+F11+E11+D11
K11 = (F382*(1+C6))+((F382^2)*((2*C2)+(2*C2*C8)))+((F382^3)*(3*C2*C4)+(3*C10*C4*C2)))
L11 = (D11/J11)*100
M11 = (G11/J11)*100
N11 = (E11/J11)*100
O11 = (H11/J11)*100
P11 = (F11/J11)*100
Q11 = (I11/J11)*100
R11 = L11+M11+N11+O11+P11+Q11
B16 = *"Coefficient of x^3"*
C16 = *"Coefficient of x^2"*
D16 = *"Coefficient of x"*
B17 = (3*C2*C4)+(3*C10*C4*C2)
C17 = (2*C2)+(2*C2*C8)
D17 = (1+C6)

The following section solves the cubic equation for [*M*] = 10^{-6} M

B25 = *"Normalized coefficient of x^3"*
C25 = *"Normalized coefficient of x^2"*
D25 = *"Normalized coefficient of x"*
E25 = *"Normalized constant"*

The coefficient of the x^3 term must be 1 in order to solve the equation. The 'normalized' values in the four cells above are obtained by dividing the cubic equation by the coefficient of x^3.

H25 = *"p"*
I25 = *"q"*
J25 = *"R"*
B26 = 1
C26 = C17/B17
D26 = D17/B17
E26 = -A2/B17
H26 = D26-((C26^2)/3)
I26 = E26-((C26*D26)/3)+((2/27)*C26^3))
J26 = ((1/27)*(H26^3))+(0.25*I26*I26)
K26 = SIGN(J26)+1
L26 = SIGN(K26)
M26 = ABS(L26-1)
I27 = -0.5*I26
J27 = SIGN(J26)*J26
J28 = SQRT(J27)
J29 = -1*J28
H30 = *"u^3 (A)"*
I30 = *"v^3 (B)"*
H31 = COMPLEX(I27,J28)
I31 = COMPLEX(I27,J29)
H32 = IMPOWER((H31,1/3)
I32 = IMPOWER(I31,1/3)
H33 = I27+J28
I33 = I27-J28
M34 = SIGN(H26)+1
N34 = SIGN(M34)
O34 = ABS(N34-1)
H35 = *"$\sqrt[3]{A}$"*
I35 = *"$\sqrt[3]{B}$"*
H36 = H33^(1/3)
I36 = I33^(1/3)
O36 = (2*O34)-1
M38 = A48*M26
F39 = *"If R is positive"*
G39 = *"If R is negative"*
M39 = M38+L26
A40 = *"w"*
B40 = *"w^2"*
E40 = *"1st Root"*
F40 = (H33^(1/3))+(I33^(1/3))-(C26/3)
G40 = B58
A41 = COMPLEX(-0.5,A43)
B41 = COMPLEX(-0.5,A44)
E41 = *"2nd Root"*
F41 = IMSUM((IMPRODUCT(A41,H36)),(IMPRODUCT(B41,I36)),(C26/-3))
G41 = C58
E42 = *"3rd Root"*
F42 = IMSUM((IMPRODUCT(B41,H36)),(IMPRODUCT(A41,I36)),(C26/-3))
G42 = D58
A43 = SQRT(3)/2
M43 = I26*M26
A44 = -A43
M44 = M43+L26
A47 = *"r"*
A48 = SQRT((-1/27)*(H26^3)*O36)
A49 = *"cos θ"*

B49 = *"θ"*
C49 = *"π"*
A50 = ((-0.5*M44)/M39)
B50 = (ACOS(A50))/((PI())*2)*360
C50 = PI()
F50 = *"Roots"*
F51 = IMSUM((IMPRODUCT(F40,L26)),(IMPRODUCT(G40,M26)))
B52 = *"θ / 3"*
F52 = IMSUM((IMPRODUCT(F41,L26)),(IMPRODUCT(G41,M26)))
B53 = B50/3
F53 = IMSUM((IMPRODUCT(F42,L26)),(IMPRODUCT(G42,M26)))
B55 = *"cos θ / 3"*
C55 = *"cos (θ + 360)/3"*
D55 = *"cos (θ + 720)/3"*
B56 = COS((B53/360)*(2*C50))
C56 = (2*(M39^(1/3))*COS((((B50+360)/3)/360)*2*C50))-(C26/3)
D56 = (2*(M39^(1/3))*COS((((B50+720)/3)/360)*2*C50))-(C26/3)
B58 = (2*(M39^(1/3))*B56)-(C26/3)
C58 = C56
D58 = D56

The following section solves the cubic equation for $[M] = 10^{-5}$ M

B61 = *"Normalized coefficient of x^3"*
C61 = *"Normalized coefficient of x^2"*
D61 = *"Normalized coefficient of x"*
E61 = *"Normalized constant"*
H61 = *"p"*
I61 = *"q"*
J61 = *"R"*
B62 = 1
C62 = C17/B17
D62 = D17/B17
E62 = -A3/B17
H62 = D62-((C62^2)/3)
I62 = E62-((C62*D62)/3)+((2/27)*C62^3))
J62 = ((1/27)*(H62^3))+(0.25*I62*I62)
K62 = SIGN(J62)+1
L62 = SIGN(K62)
M62 = ABS(L62-1)
I63 = -0.5*I62
J63 = SIGN(J62)*J62
J64 = SQRT(J63)
J65 = -1*J64
H66 = *"u^3 (A)"*
I66 = *"v^3 (B)"*
H67 = COMPLEX(I63,J64)
I67 = COMPLEX(I63,J65)
H68 = IMPOWER((H67,1/3)
I68 = IMPOWER(I67,1/3)
H69 = I63+J64
I69 = I63-J64
M70 = SIGN(H62)+1
N70 = SIGN(M70)
O70 = ABS(N70-1)
H71 = *"$\sqrt[3]{A}$"*
I71 = *"$\sqrt[3]{B}$"*
H72 = H69^(1/3)
I72 = I69^(1/3)
O72 = (2*O70)-1
M74 = A84*M62
F75 = *"If R is positive"*
G75 = *"If R is negative"*
M75 = M74+L62
A76 = *"w"*

B76 = *"w²"*
E76 = *"1st Root"*
F76 = (H69^(1/3))+(I69^(1/3))-(C62/3)
G76 = B94
A77 = COMPLEX(-0.5,A79)
B77 = COMPLEX(-0.5,A80)
E77 = *"2nd Root"*
F77 = IMSUM((IMPRODUCT(A77,H72)),(IMPRODUCT(B77,I72)),(C62/-3))
G77 = C94
E78 = *"3rd Root"*
F78 = IMSUM((IMPRODUCT(B77,H72)),(IMPRODUCT(A77,I72)),(C62/-3))
G78 = D94
A79 = SQRT(3)/2
M79 = I62*M62
A80 = -A79
M80 = M79+L62
A83 = *"r"*
A84 = SQRT((-1/27)*(H62^3)*O72)
A85 = *"cos θ"*
B85 = *"θ"*
C85 = *"π"*
A86 = ((-0.5*M80)/M75)
B86 = (ACOS(A86))/((PI())*2)*360
C86 = PI()
F86 = *"Roots"*
F87 = IMSUM((IMPRODUCT(F76,L62)),(IMPRODUCT(G76,M62)))
B88 = *"θ / 3"*
F88 = IMSUM((IMPRODUCT(F77,L62)),(IMPRODUCT(G77,M62)))
B89 = B86/3
F89 = IMSUM((IMPRODUCT(F78,L62)),(IMPRODUCT(G78,M62)))
B91 = *"cos θ / 3"*
C91 = *"cos (θ + 360)/3"*
D91 = *"cos (θ + 720)/3"*
B92 = COS((B89/360)*(2*C86))
C92 = (2*(M75^(1/3))*COS((((B86+360)/3)/360)*2*C86))-(C62/3)
D92 = (2*(M75^(1/3))*COS((((B86+720)/3)/360)*2*C86))-(C62/3)
B94 = 2*(M75^(1/3))*B92)-(C62/3)
C94 = C92
D94 = D92

The following section solves the cubic equation for $[M] = 10^{-4}$ M

B98 = *"Normalized coefficient of x³"*
C98 = *"Normalized coefficient of x²"*
D98 = *"Normalized coefficient of x"*
E98 = *"Normalized constant"*
H98 = *"p"*
I98 = *"q"*
J98 = *"R"*
B99 = 1
C99 = C17/B17
D99 = D17/B17
E99 = -A4/B17
H99 = D99-((C99^2)/3)
I99 = E99-((C99*D99)/3)+((2/27)*C99^3))
J99 = ((1/27)*(H99^3))+(0.25*I99*I99)
K99 = SIGN(J99)+1
L99 = SIGN(K99)
M99 = ABS(L99-1)
I100 = -0.5*I99
J100 = SIGN(J99)*J99
J101 = SQRT(J100)
J102 = -1*J101
H103 = *"u³ (A)"*
I103 = *"v³ (B)"*

H104 = COMPLEX(I100,J101)
I104 = COMPLEX(I100,J102)
H105 = IMPOWER((H104,1/3)
I105 = IMPOWER(I104,1/3)
H106 = I100+J101
I106 = I100-J101
M107 = SIGN(H99)+1
N107 = SIGN(M107)
O107 = ABS(N107-1)
H108 = *"$\sqrt[3]{A}$"*
I108 = *"$\sqrt[3]{B}$"*
H109 = H106^(1/3)
I109 = I106^(1/3)
O109 = (2*O107)-1
M111 = A121*M99
F112 = *"If R is positive"*
G112 = *"If R is negative"*
M112 = M111+L99
A113 = *"w"*
B113 = *"w^2"*
E113 = *"1st Root"*
F113 = (H106^(1/3))+(I106^(1/3))-(C99/3)
G113 = B131
A114 = COMPLEX(-0.5,A116)
B114 = COMPLEX(-0.5,A117)
E114 = *"2nd Root"*
F114 = IMSUM((IMPRODUCT(A114,H109)),(IMPRODUCT(B114,I109)),(C99/-3))
G114 = C131
E115 = *"3rd Root"*
F115 = IMSUM((IMPRODUCT(B114,H109)),(IMPRODUCT(A114,I109)),(C99/-3))
G115 = D131
A116 = SQRT(3)/2
M116 = I99*M99
A117 = -A116
M117 = M116+L99
A120 = *"r"*
A121 = SQRT((-1/27)*(H99^3)*O109)
A122 = *"cos θ"*
B122 = *"θ"*
C122 = *"π"*
A123 = ((-0.5*M117)/M112)
B123 = (ACOS(A123))/((PI())*2)*360
C123 = PI()
F123 = *"Roots"*
F124 = IMSUM((IMPRODUCT(F113,L99)),(IMPRODUCT(G113,M99)))
B125 = *"θ / 3"*
F125 = IMSUM((IMPRODUCT(F114,L99)),(IMPRODUCT(G114,M99)))
B126 = *B123/3*
F126 = IMSUM((IMPRODUCT(F115,L99)),(IMPRODUCT(G115,M99)))
B128 = *"cos θ / 3"*
C128 = *"cos (θ + 360)/3"*
D128 = *"cos (θ + 720)/3"*
B129 = COS((B126/360)*(2*C123))
C129 = (2*(M112^(1/3))*COS((((B123+360)/3)/360)*2*C123))-(C99/3)
D129 = (2*(M112^(1/3))*COS((((B123+720)/3)/360)*2*C123))-(C99/3)
B131 = (2*(M112^(1/3))*B129)-(C99/3)
C131 = C129
D131 = D129

The following section solves the cubic equation for $[M] = 10^{-3}$ M

B135 = *"Normalized coefficient of x^3"*
C135 = *"Normalized coefficient of x^2"*
D135 = *"Normalized coefficient of x"*
E135 = *"Normalized constant"*

```
H135  =  "p"
I135  =  "q"
J135  =  "R"
B136  =  1
C136  =  C17/B17
D136  =  D17/B17
E136  =  -A5/B17
H136  =  D136-((C136^2)/3)
I136  =  E136-((C136*D136)/3)+((2/27)*C136^3))
J136  =  ((1/27)*(H136^3))+(0.25*I136*I136)
K136  =  SIGN(J136)+1
L136  =  SIGN(K136)
M136  =  ABS(L136-1)
I137  =  -0.5*I136
J137  =  SIGN(J136)*J136
J138  =  SQRT(J137)
J139  =  -1*J138
H140  =  "u³ (A)"
I140  =  "v³ (B)"
H141  =  COMPLEX(I137,J138)
I141  =  COMPLEX(I137,J139)
H142  =  IMPOWER((H141,1/3)
I142  =  IMPOWER(I141,1/3)
H143  =  I137+J138
I143  =  I137-J138
M144  =  SIGN(H136)+1
N144  =  SIGN(M144)
O144  =  ABS(N144-1)
H145  =  "³√A"
I145  =  "³√B"
H146  =  H143^(1/3)
I146  =  I143^(1/3)
O146  =  (2*O144)-1
M148  =  A158*M136
F149  =  "If R is positive"
G149  =  "If R is negative"
M149  =  M148+L126
A150  =  "w"
B150  =  "w²"
E150  =  "1st Root"
F150  =  (H143^(1/3))+(I143^(1/3))-(C136/3)
G150  =  B168
A151  =  COMPLEX(-0.5,A153)
B151  =  COMPLEX(-0.5,A154)
E151  =  "2nd Root"
F151  =  IMSUM((IMPRODUCT(A151,H146)),(IMPRODUCT(B151,I146)),(C136/-3))
G151  =  C168
E152  =  "3rd Root"
F152  =  IMSUM((IMPRODUCT(B151,H146)),(IMPRODUCT(A151,I146)),(C136/-3))
G152  =  D168
A153  =  SQRT(3)/2
M153  =  I136*M136
A154  =  -A153
M154  =  M153+L136
A157  =  "r"
A158  =  SQRT((-1/27)*(H136^3)*O146)
A159  =  "cos θ"
B159  =  "θ"
C159  =  "π"
A160  =  ((-0.5*M154)/M149)
B160  =  (ACOS(A160))/((PI())*2)*360
C160  =  PI()
F160  =  "Roots"
F161  =  IMSUM((IMPRODUCT(F150,L136)),(IMPRODUCT(G150,M136)))
```

B162 = *"θ / 3"*
F162 = IMSUM((IMPRODUCT(F151,L136)),(IMPRODUCT(G151,M136)))
B163 = B160/3
F163 = IMSUM((IMPRODUCT(F152,L136)),(IMPRODUCT(G152,M136)))
B165 = *"cos θ / 3"*
C165 = *"cos (θ + 360)/3"*
D165 = *"cos (θ + 720)/3"*
B166 = COS((B163/360)*(2*C160))
C166 = (2*(M149^(1/3))*COS((((B160+360)/3)/360)*2*C160))-(C136/3)
D166 = (2*(M149^(1/3))*COS((((B160+720)/3)/360)*2*C160))-(C136/3)
B168 = (2*(M149^(1/3))*B166)-(C136/3)
C168 = C166
D168 = D166

The following section solves the cubic equation for $[M] = 10^{-2}$ M

B171 = *"Normalized coefficient of x^3"*
C171 = *"Normalized coefficient of x^2"*
D171 = *"Normalized coefficient of x"*
E171 = *"Normalized constant"*
H171 = *"p"*
I171 = *"q"*
J171 = *"R"*
B172 = 1
C172 = C17/B17
D172 = D17/B17
E172 = -A6/B17
H172 = D172-((C172^2)/3)
I172 = E172-((C172*D172)/3)+((2/27)*C172^3))
J172 = ((1/27)*(H172^3))+(0.25*I172*I172)
K172 = SIGN(J172)+1
L172 = SIGN(K172)
M172 = ABS(L172-1)
I173 = -0.5*I172
J173 = SIGN(J172)*J172
J174 = SQRT(J173)
J175 = -1*J174
H176 = *"u^3 (A)"*
I176 = *"v^3 (B)"*
H177 = COMPLEX(I173,J174)
I177 = COMPLEX(I173,J175)
H178 = IMPOWER((H177,1/3)
I178 = IMPOWER(I177,1/3)
H179 = I173+J174
I179 = I173-J174
M180 = SIGN(H172)+1
N180 = SIGN(M180)
O180 = ABS(N180-1)
H181 = *"$\sqrt[3]{A}$"*
I181 = *"$\sqrt[3]{B}$"*
H182 = H179^(1/3)
I182 = I179^(1/3)
O182 = (2*O180)-1
M184 = A194*M172
F185 = *"If R is positive"*
G185 = *"If R is negative"*
M185 = M184+L172
A186 = *"w"*
B186 = *"w^2"*
E186 = *"1st Root"*
F186 = (H179^(1/3))+(I179^(1/3))-(C172/3)
G186 = B204
A187 = COMPLEX(-0.5,A189)
B187 = COMPLEX(-0.5,A190)

E187 = *"2nd Root"*
F187 = IMSUM((IMPRODUCT(A187,H182)),(IMPRODUCT(B187,I182)),(C172/-3))
G187 = C204
E188 = *"3rd Root"*
F188 = IMSUM((IMPRODUCT(B187,H182)),(IMPRODUCT(A187,I182)),(C172/-3))
G188 = D204
A189 = SQRT(3)/2
M189 = I172*M172
A190 = -A189
M190 = M189+L172
A193 = *"r"*
A194 = SQRT((-1/27)*(H172^3)*O182)
A195 = *"cos θ"*
B195 = *"θ"*
C195 = *"π"*
A196 = ((-0.5*M190)/M185)
B196 = (ACOS(A196))/((PI())*2)*360
C196 = PI()
F196 = *"Roots"*
F197 = IMSUM((IMPRODUCT(F186,L172)),(IMPRODUCT(G186,M172)))
B198 = *"θ / 3"*
F198 = IMSUM((IMPRODUCT(F187,L172)),(IMPRODUCT(G187,M172)))
B199 = B196/3
F199 = IMSUM((IMPRODUCT(F188,L172)),(IMPRODUCT(G188,M172)))
B201 = *"cos θ / 3"*
C201 = *"cos (θ + 360)/3"*
D201 = *"cos (θ + 720)/3"*
B202 = COS((B199/360)*(2*C196))
C202 = (2*(M185^(1/3))*COS((((B196+360)/3)/360)*2*C196))-(C172/3)
D202 = (2*(M185^(1/3))*COS((((B196+720)/3)/360)*2*C196))-(C172/3)
B204 = (2*(M185^(1/3))*B202)-(C172/3)
C204 = C202
D204 = D202

The following section solves the cubic equation for $[M] = 10^{-1}$ M

B208 = *"Normalized coefficient of x^3"*
C208 = *"Normalized coefficient of x^2"*
D208 = *"Normalized coefficient of x"*
E208 = *"Normalized constant"*
H208 = *"p"*
I208 = *"q"*
J208 = *"R"*
B209 = 1
C209 = C17/B17
D209 = D17/B17
E209 = -A7/B17
H209 = D209-((C209^2)/3)
I209 = E209-((C209*D209)/3)+((2/27)*C209^3))
J209 = ((1/27)*(H209^3))+(0.25*I209*I209)
K209 = SIGN(J209)+1
L209 = SIGN(K209)
M209 = ABS(L209-1)
I210 = -0.5*I209
J210 = SIGN(J209)*J209
J211 = SQRT(J210)
J212 = -1*J211
H213 = *"u^3 (A)"*
I213 = *"v^3 (B)"*
H214 = COMPLEX(I210,J211)
I214 = COMPLEX(I210,J212)
H215 = IMPOWER((H214,1/3)
I215 = IMPOWER(I214,1/3)
H216 = I210+J211
I216 = I210-J211

M217 = SIGN(H209)+1
N217 = SIGN(M217)
O217 = ABS(N217-1)
H218 = *"$\sqrt[3]{A}$"*
I218 = *"$\sqrt[3]{B}$"*
H219 = H216^(1/3)
I219 = I216^(1/3)
O219 = (2*O217)-1
M221 = A231*M209
F222 = *"If R is positive"*
G222 = *"If R is negative"*
M222 = M221+L209
A223 = *"w"*
B223 = *"w^2"*
E223 = *"1st Root"*
F223 = (H216^(1/3))+(I216^(1/3))-(C209/3)
G223 = B241
A224 = COMPLEX(-0.5,A226)
B224 = COMPLEX(-0.5,A227)
E224 = *"2nd Root"*
F224 = IMSUM((IMPRODUCT(A224,H219)),(IMPRODUCT(B224,I219)),(C209/-3))
G224 = C241
E225 = *"3rd Root"*
F225 = IMSUM((IMPRODUCT(B224,H219)),(IMPRODUCT(A224,I219)),(C209/-3))
G225 = D241
A226 = SQRT(3)/2
M226 = I209*M209
A227 = -A226
M227 = M226+L209
A230 = *"r"*
A231 = SQRT((-1/27)*(H209^3)*O219)
A232 = *"cos θ"*
B232 = *"θ"*
C232 = *"π"*
A233 = ((-0.5*M227)/M222)
B233 = (ACOS(A233))/((PI())*2)*360
C233 = PI()
F233 = *"Roots"*
F234 = IMSUM((IMPRODUCT(F223,L209)),(IMPRODUCT(G223,M209)))
B235 = *"θ / 3"*
F235 = IMSUM((IMPRODUCT(F224,L209)),(IMPRODUCT(G224,M209)))
B236 = B233/3
F236 = IMSUM((IMPRODUCT(F225,L209)),(IMPRODUCT(G225,M209)))
B238 = *"cos θ / 3"*
C238 = *"cos (θ + 360)/3"*
D238 = *"cos (θ + 720)/3"*
B239 = COS((B236/360)*(2*C233))
C239 = (2*(M222^(1/3))*COS((((B233+360)/3)/360)*2*C233))-(C209/3)
D239 = (2*(M222^(1/3))*COS((((B233+720)/3)/360)*2*C233))-(C209/3)
B241 = (2*(M222^(1/3))*B239)-(C209/3)
C241 = C239
D241 = D239

The following section solves the cubic equation for [*M*] = 1 M

B245 = *"Normalized coefficient of x^3"*
C245 = *"Normalized coefficient of x^2"*
D245 = *"Normalized coefficient of x"*
E245 = *"Normalized constant"*
H245 = *"p"*
I245 = *"q"*
J245 = *"R"*
B246 = 1
C246 = C17/B17
D246 = D17/B17

E246 = -A8/B17
H246 = D246-((C246^2)/3)
I246 = E246-((C246*D246)/3)+((2/27)*C246^3))
J246 = ((1/27)*(H246^3))+(0.25*I246*I246)
K246 = SIGN(J246)+1
L246 = SIGN(K246)
M246 = ABS(L246-1)
I247 = -0.5*I246
J247 = SIGN(J246)*J246
J248 = SQRT(J247)
J249 = -1*J248
H250 = *"u^3 (A)"*
I250 = *"v^3 (B)"*
H251 = COMPLEX(I247,J248)
I251 = COMPLEX(I247,J249)
H252 = IMPOWER((H251,1/3)
I252 = IMPOWER(I251,1/3)
H253 = I247+J248
I253 = I247-J248
M254 = SIGN(H246)+1
N254 = SIGN(M254)
O254 = ABS(N254-1)
H255 = *"$\sqrt[3]{A}$"*
I255 = *"$\sqrt[3]{B}$"*
H256 = H253^(1/3)
I256 = I253^(1/3)
O256 = (2*O254)-1
M258 = A268*M246
F259 = *"If R is positive"*
G259 = *"If R is negative"*
M259 = M258+L246
A260 = *"w"*
B260 = *"w^2"*
E260 = *"1st Root"*
F260 = (H253^(1/3))+(I253^(1/3))-(C246/3)
G260 = B278
A261 = COMPLEX(-0.5,A263)
B260 = COMPLEX(-0.5,A264)
E261 = *"2nd Root"*
F261 = IMSUM((IMPRODUCT(A261,H256)),(IMPRODUCT(B261,I256)),(C246/-3))
G261 = C278
E262 = *"3rd Root"*
F262 = IMSUM((IMPRODUCT(B261,H256)),(IMPRODUCT(A261,I256)),(C246/-3))
G262 = D278
A263 = SQRT(3)/2
M263 = I246*M246
A264 = -A263
M264 = M263+L246
A267 = *"r"*
A268 = SQRT((-1/27)*(H246^3)*O256)
A269 = *"cos θ"*
B269 = *"θ"*
C269 = *"π"*
A270 = ((-0.5*M264)/M259)
B270 = (ACOS(A270))/((PI())*2)*360
C270 = PI()
F270 = *"Roots"*
F271 = IMSUM((IMPRODUCT(F260,L246)),(IMPRODUCT(G260,M246)))
B272 = *"θ / 3"*
F272 = IMSUM((IMPRODUCT(F261,L246)),(IMPRODUCT(G261,M246)))
B273 = B270/3
F273 = IMSUM((IMPRODUCT(F262,L246)),(IMPRODUCT(G262,M246)))
B275 = *"cos θ / 3"*
C275 = *"cos (θ + 360)/3"*
D275 = *"cos (θ + 720)/3"*

B276 = COS((B273/360)*(2*C270))
C276 = (2*(M259^(1/3))*COS((((B270+360)/3)/360)*2*C270))-(C246/3)
D276 = (2*(M259^(1/3))*COS((((B270+720)/3)/360)*2*C270))-(C246/3)
B278 = (2*(M259^(1/3))*B276)-(C246/3)
C278 = C276
D278 = D276

The following section solves the cubic equation for [*M*] = 10 M

B283 = *"Normalized coefficient of x^3"*
C283 = *"Normalized coefficient of x^2"*
D283 = *"Normalized coefficient of x"*
E283 = *"Normalized constant"*
H283 = *"p"*
I283 = *"q"*
J283 = *"R"*
B284 = 1
C284 = C17/B17
D284 = D17/B17
E284 = -A9/B17
H284 = D284-((C284^2)/3)
I284 = E284-((C284*D284)/3)+((2/27)*C284^3))
J284 = ((1/27)*(H284^3))+(0.25*I284*I284)
K284 = SIGN(J284)+1
L284 = SIGN(K284)
M284 = ABS(L284-1)
I285 = -0.5*I284
J285 = SIGN(J284)*J284
J286 = SQRT(J285)
J287 = -1*J286
H288 = *"u^3 (A)"*
I288 = *"v^3 (B)"*
H289 = COMPLEX(I285,J286)
I289 = COMPLEX(I285,J287)
H290 = IMPOWER((H289,1/3)
I290 = IMPOWER(I289,1/3)
H291 = I285+J286
I291 = I285-J286
M292 = SIGN(H284)+1
N292 = SIGN(M292)
O292 = ABS(N292-1)
H293 = *"$\sqrt[3]{A}$"*
I293 = *"$\sqrt[3]{B}$"*
H294 = H291^(1/3)
I294 = I291^(1/3)
O294 = (2*O292)-1
M296 = A306*M284
F297 = *"If R is positive"*
G297 = *"If R is negative"*
M297 = M296+L284
A298 = *"w"*
B298 = *"w^2"*
E298 = *"1st Root"*
F298 = (H291^(1/3))+(I291^(1/3))-(C284/3)
G298 = B316
A299 = COMPLEX(-0.5,A301)
B299 = COMPLEX(-0.5,A302)
E299 = *"2nd Root"*
F299 = IMSUM((IMPRODUCT(A299,H294)),(IMPRODUCT(B299,I294)),(C284/-3))
G299 = C316
E300 = *"3rd Root"*
F300 = IMSUM((IMPRODUCT(B299,H294)),(IMPRODUCT(A299,I294)),(C284/-3))
G300 = D316
A301 = SQRT(3)/2
M301 = I284*M284

A302 = -A301
M302 = M301+L284
A305 = *"r"*
A306 = SQRT((-1/27)*(H284^3)*O294)
A307 = *"cos θ"*
B307 = *"θ"*
C307 = *"π"*
A308 = ((-0.5*M302)/M297)
B308 = (ACOS(A308))/((PI())*2)*360
C308 = PI()
F308 = *"Roots"*
F309 = IMSUM((IMPRODUCT(F298,L284)),(IMPRODUCT(G298,M284)))
B310 = *"θ / 3"*
F310 = IMSUM((IMPRODUCT(F299,L284)),(IMPRODUCT(G299,M284)))
B311 = B308/3
F311 = IMSUM((IMPRODUCT(F300,L284)),(IMPRODUCT(G300,M284)))
B313 = *"cos θ / 3"*
C313 = *"cos (θ + 360)/3"*
D313 = *"cos (θ + 720)/3"*
B314 = COS((B311/360)*(2*C308))
C314 = (2*(M297^(1/3))*COS((((B308+360)/3)/360)*2*C308))-(C284/3)
D314 = (2*(M297^(1/3))*COS((((B308+720)/3)/360)*2*C308))-(C284/3)
B316 = (2*(M297^(1/3))*B314)-(C284/3)
C316 = C314
D316 = D314

The following section solves the cubic equation for [*M*] = 100 M

B320 = *"Normalized coefficient of x^3"*
C320 = *"Normalized coefficient of x^2"*
D320 = *"Normalized coefficient of x"*
E320 = *"Normalized constant"*
H320 = *"p"*
I320 = *"q"*
J320 = *"R"*
B321 = 1
C321 = C17/B17
D321 = D17/B17
E321 = -A10/B17
H321 = D321-((C321^2)/3)
I321 = E321-((C321*D321)/3)+((2/27)*C321^3))
J321 = ((1/27)*(H321^3))+(0.25*I321*I321)
K321 = SIGN(J321)+1
L321 = SIGN(K321)
M321 = ABS(L321-1)
I322 = -0.5*I321
J322 = SIGN(J321)*J321
J323 = SQRT(J322)
J324 = -1*J323
H325 = *"u^3 (A)"*
I325 = *"v^3 (B)"*
H326 = COMPLEX(I322,J323)
I326 = COMPLEX(I322,J324)
H327 = IMPOWER((H326,1/3)
I327 = IMPOWER(I326,1/3)
H328 = I322+J323
I328 = I322-J323
M329 = SIGN(H321)+1
N329 = SIGN(M329)
O329 = ABS(N329-1)
H330 = *"$\sqrt[3]{A}$"*
I330 = *"$\sqrt[3]{B}$"*
H331 = H228^(1/3)
I331 = I328^(1/3)
O331 = (2*O329)-1

M336 = A343*M321
F334 = *"If R is positive"*
G334 = *"If R is negative"*
M334 = M333+L321
A335 = *"w"*
B335 = *"w²"*
E335 = *"1st Root"*
F335 = (H328^(1/3))+(I328^(1/3))-(C321/3)
G335 = B353
A336 = COMPLEX(-0.5,A338)
B336 = COMPLEX(-0.5,A339)
E336 = *"2nd Root"*
F336 = IMSUM((IMPRODUCT(A336,H331)),(IMPRODUCT(B336,I331)),(C321/-3))
G336 = C353
E337 = *"3rd Root"*
F337 = IMSUM((IMPRODUCT(B336,H331)),(IMPRODUCT(A336,I331)),(C321/-3))
G337 = D353
A338 = SQRT(3)/2
M338 = I321*M321
A339 = -A338
M339 = M338+L321
A342 = *"r"*
A343 = SQRT((-1/27)*(H321^3)*O331)
A344 = *"cos θ"*
B344 = *"θ"*
C344 = *"π"*
A345 = ((-0.5*M339)/M334)
B345 = (ACOS(A345))/((PI())*2)*360
C345 = PI()
F345 = *"Roots"*
F346 = IMSUM((IMPRODUCT(F335,L321)),(IMPRODUCT(G335,M321)))
B347 = *"θ / 3"*
F347 = IMSUM((IMPRODUCT(F336,L321)),(IMPRODUCT(G336,M321)))
B348 = B345/3
F348 = IMSUM((IMPRODUCT(F337,L321)),(IMPRODUCT(G337,M321)))
B350 = *"cos θ / 3"*
C350 = *"cos (θ + 360)/3"*
D350 = *"cos (θ + 720)/3"*
B351 = COS((B348/360)*(2*C345))
C351 = (2*(M334^(1/3))*COS((((B345+360)/3)/360)*2*C345))-(C321/3)
D351 = (2*(M334^(1/3))*COS((((B345+720)/3)/360)*2*C345))-(C321/3)
B353 = (2*(M334^(1/3))*B351)-(C321/3)
C353 = C351
D353 = D351

The following section solves the cubic equation for the value of [*M*] entered into A11

B356 = *"Normalized coefficient of x³"*
C356 = *"Normalized coefficient of x²"*
D356 = *"Normalized coefficient of x"*
E356 = *"Normalized constant"*
H356 = *"p"*
I356 = *"q"*
J356 = *"R"*
B357 = 1
C357 = C17/B17
D357 = D17/B17
E357 = -A11/B17
H357 = D357-((C357^2)/3)
I357 = E357-((C357*D357)/3)+((2/27)*C357^3))
J357 = ((1/27)*(H357^3))+(0.25*I357*I357)
K357 = SIGN(J357)+1
L357 = SIGN(K357)
M357 = ABS(L357-1)
I358 = -0.5*I357

J358 = SIGN(J357)*J357
J359 = SQRT(J358)
J360 = -1*J359
H361 = *"u^3 (A)"*
I361 = *"v^3 (B)"*
H362 = COMPLEX(I358,J359)
I362 = COMPLEX(I358,J360)
H363 = IMPOWER((H362,1/3)
I363 = IMPOWER(I362,1/3)
H364 = I358+J359
I364 = I358-J359
M365 = SIGN(H357)+1
N365 = SIGN(M365)
O365 = ABS(N365-1)
H366 = *"$\sqrt[3]{A}$"*
I366 = *"$\sqrt[3]{B}$"*
H367 = H264^(1/3)
I367 = I364^(1/3)
O367 = (2*O365)-1
M369 = A379*M357
F370 = *"If R is positive"*
G370 = *"If R is negative"*
M370 = M369+L357
A371 = *"w"*
B371 = *"w^2"*
E371 = *"1st Root"*
F371 = (H364^(1/3))+(I364^(1/3))-(C357/3)
G371 = B389
A372 = COMPLEX(-0.5,A374)
B372 = COMPLEX(-0.5,A375)
E372 = *"2nd Root"*
F372 = IMSUM((IMPRODUCT(A372,H367)),(IMPRODUCT(B372,I367)),(C357/-3))
G372 = C389
E373 = *"3rd Root"*
F373 = IMSUM((IMPRODUCT(B372,H367)),(IMPRODUCT(A372,I367)),(C357/-3))
G373 = D389
A374 = SQRT(3)/2
M374 = I357*M357
A375 = -A374
M375 = M374+L357
A378 = *"r"*
A379 = SQRT((-1/27)*(H357^3)*O367)
A380 = *"cos θ"*
B380 = *"θ"*
C380 = *"π"*
A381 = ((-0.5*M375)/M370)
B381 = (ACOS(A381))/((PI())*2)*360
C381 = PI()
F381 = *"Roots"*
F382 = IMSUM((IMPRODUCT(F371,L357)),(IMPRODUCT(G371,M357)))
B383 = *"θ / 3"*
F383 = IMSUM((IMPRODUCT(F372,L357)),(IMPRODUCT(G372,M357)))
B384 = B381/3
F384 = IMSUM((IMPRODUCT(F373,L357)),(IMPRODUCT(G373,M357)))
B386 = *"cos θ / 3"*
C386 = *"cos (θ + 360)/3"*
D386 = *"cos (θ + 720)/3"*
B387 = COS((B384/360)*(2*C381))
C387 = (2*(M370^(1/3))*COS((((B381+360)/3)/360)*2*C381))-(C357/3)
D387 = (2*(M370^(1/3))*COS((((B381+720)/3)/360)*2*C381))-(C357/3)
B389 = (2*(M370^(1/3))*B387)-(C357/3)
C389 = C387
D389 = D387

The output from this spreadsheet is a plot of how the concentration of each monomer/oligomer present in solution varies with the concentration of dissolved monomer. The *x* axis is a log scale of the dissolved monomer concentration [*M*], and the *y* axis is the percentage of any one particular species expressed as its molar concentration divided by the total concentration of all species present in solution. It should be noted that the sum total of the concentrations of all species present in solution will be less than the value of [*M*], unless there is no oligomerization whatsoever, in which case the value will, obviously, be [*M*]. For example, if 100 mM of monomer is dissolved in solution, and forms exclusively the [*c*2]daisy chain, the total concentration of all species present in solution is 50 mM. The *x* values are taken from cells B2–10, and the six sets of *y* axis data originate from cells L2–10, M2–10, N2–10, O2–10, P2–10, Q2–10, respectively.

References and Notes

1. This model—for simplicity's sake—also assumes that only one stereoisomeric cyclic dimer, and only one stereoisomeric cyclic trimer are formed.
2. Ashton, P. R.; Bartsch, R. A.; Cantrill, S. J.; Hanes, Jr., R. E.; Hickingbottom, S. K.; Lowe, J. N.; Preece, J. A.; Stoddart, J. F.; Talanov, V. S.; Wang, Z.-H. *Tetrahedron Lett.* **1999**, *40*, 3661–3664.
3. The conclusion that lower values of K_a (especially K_{a1}) than those observed in model systems fit better the experimental data observed here may reflect the fact that oligomerization of this self-complementary system always requires bringing together two positively charged species. This repulsive Coulombic effect may serve to reduce the overall affinity for two daisy chain monomers in comparison with the model two component system, in which a *cationic* thread is bound by a *neutral* macrocycle.

$K_{c1} = [c1] / [a1]$ (1) $\therefore$ $[c1] = K_{c1}[a1]$ (6)

$K_{c2} = [c2] / [a2]$ (2) $\therefore$ $[c2] = K_{c2}K_{a2}[a1]^2$ (7)

$K_{c3} = [c3] / [a3]$ (3) $\therefore$ $[c3] = K_{c3}K_{a3}K_{a2}[a1]^3$ (8)

$K_{a2} = [a2] / [a1]^2$ (4) $\therefore$ $[a2] = K_{a2}[a1]^2$ (9)

$K_{a3} = [a3] / ([a1][a2])$ (5) $\therefore$ $[a3] = K_{a3}K_{a2}[a1]^3$ (10)

$[M]$ = concentration of monomer dissolved in solution

$$[M] = [a1] + [c1] + 2[a2] + 2[c2] + 3[a3] + 3[c3] \quad (11)$$

$$[M] = (3K_{c3}K_{a3}K_{a2} + 3K_{a3}K_{a2})[a1]^3 + (2K_{c2}K_{a2} + 2K_{a2})[a1]^2 + (1 + K_{c1})[a1] \quad (12)$$

$$(3K_{c3}K_{a3}K_{a2} + 3K_{a3}K_{a2})[a1]^3 + (2K_{c2}K_{a2} + 2K_{a2})[a1]^2 + (1 + K_{c1})[a1] - [M] = 0 \quad (13)$$

Equations

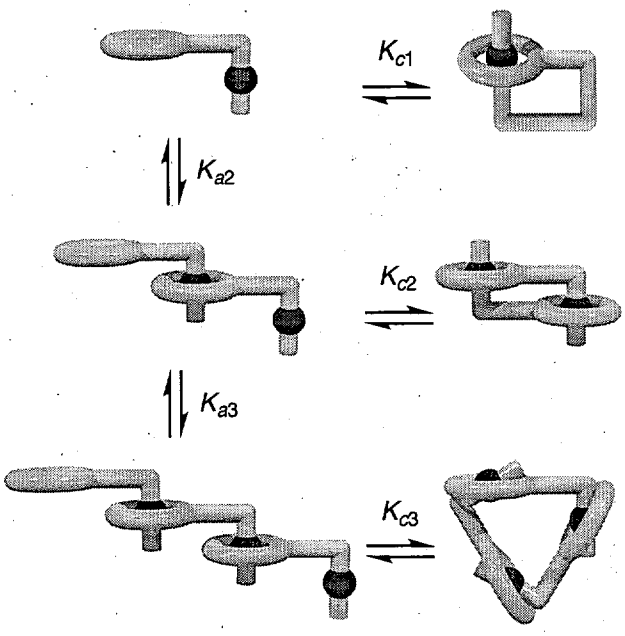


Figure S1. A schematic representation of the dynamic assembly of both acyclic and cyclic daisy chain superstructures (up to, and including, trimers) from a self-complementary monomer.

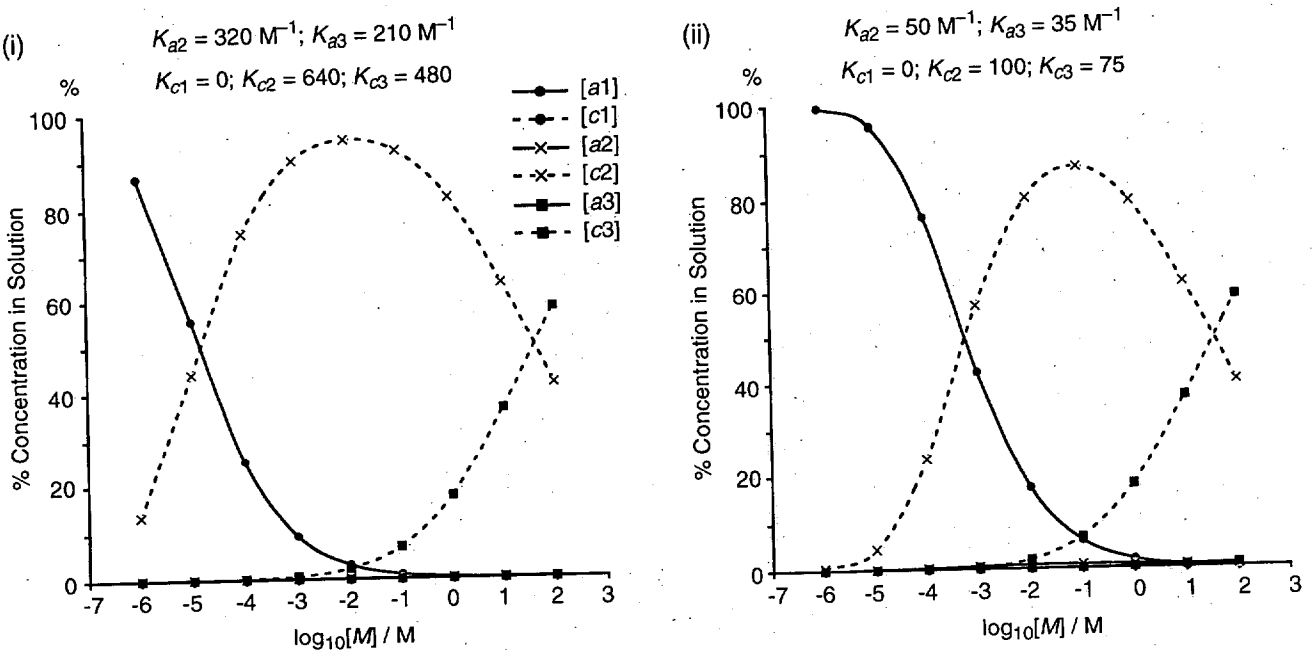


Figure S2. Concentration profiles—plotted using an Excel spreadsheet—that demonstrate how, based upon assumed K_a values, the concentration of daisy chain species in solution (expressed as a % of the total concentration of all species in solution) varies with the initial concentration of dissolved monomer (M).

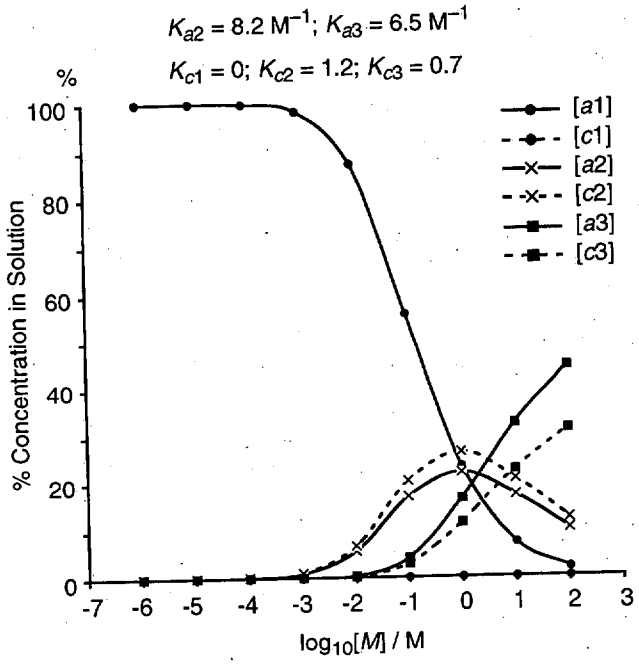


Figure S3. A concentration profile can be constructed for **29**-H·PF_6 based upon the K_a values determined from the ^{19}F NMR spectroscopic studies.

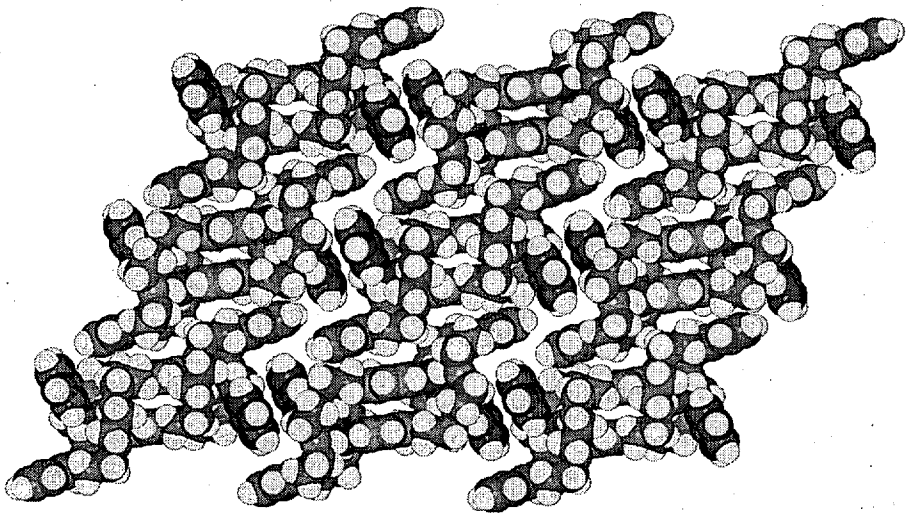


Figure S3. The mosaic-like sheet of dimer pairs formed by **1**-H^+. This supramolecular sheet self-assembles *via*, in one direction (Figure S4), a combination of face-to-face π–π stacking of the terminal phenyl rings of each monomer (interplanar and centroid-centroid separations of 3.62 and 3.73 Å, respectively) and edge-to-face aromatic interactions between these pairs of interacting terminal rings and the immediately adjacent unsubstituted catechol rings of neighboring dimer pairs (centroid-centroid separation is 5.06 Å, the rings being inclined by 83° to each other). Adjacent rows of supermolecules are aligned such that pairs of *O*-methylene hydrogen atoms within the polyether linkages in one π-stacked row are directed from above and below into the π-faces of the already π–π stacked substituted catechol rings within each dimer, producing the array depicted in Figure S5. The [H···π] distances are 2.69 Å and the associated [C–H···π] angles are 161°. Channels are formed between adjacent sheets, which are populated by trifluoroacetate and trifluoroacetic acid counterions / solvent molecules.

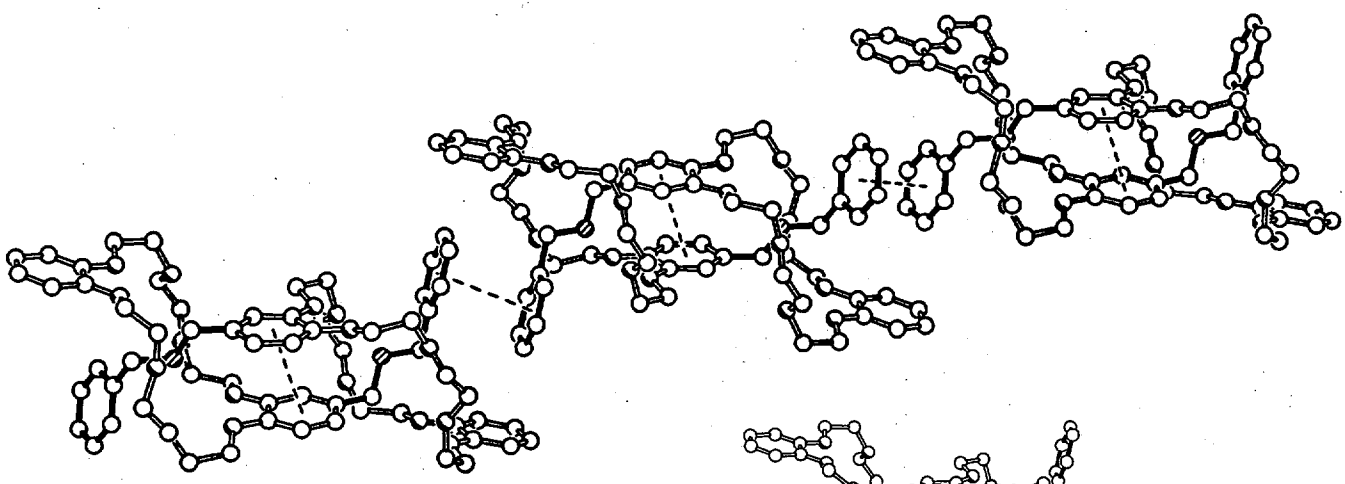


Figure S4. The packing of dimers of **1**-H^+, in one direction, *via* face-to-face π-π stacking interactions and edge-to-face aromatic interactions.

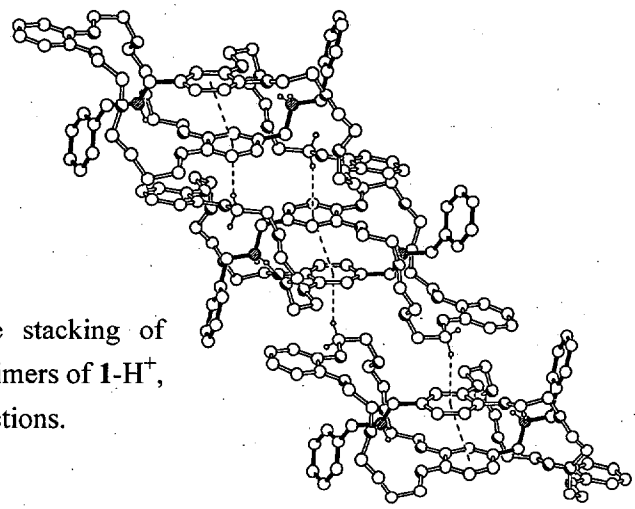


Figure S5. The stacking of adjacent rows of dimers of **1**-H^+, *via* C–H···π interactions.

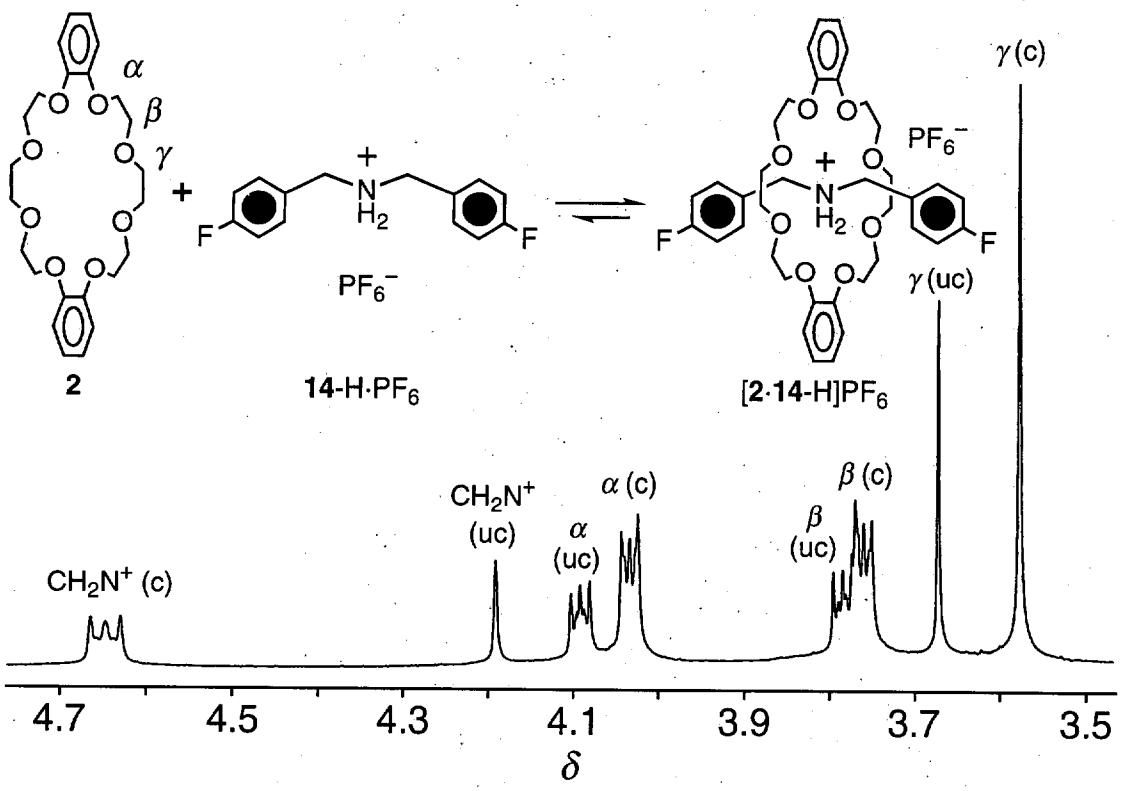


Figure S6. The partial ^{1}H NMR spectrum (400 MHz, 300 K) of a CD_3CN solution containing a 1:1 mixture of DB24C8 (**2**) and the *p*-F-substituted dibenzylammonium salt **14**-H·PF_6.

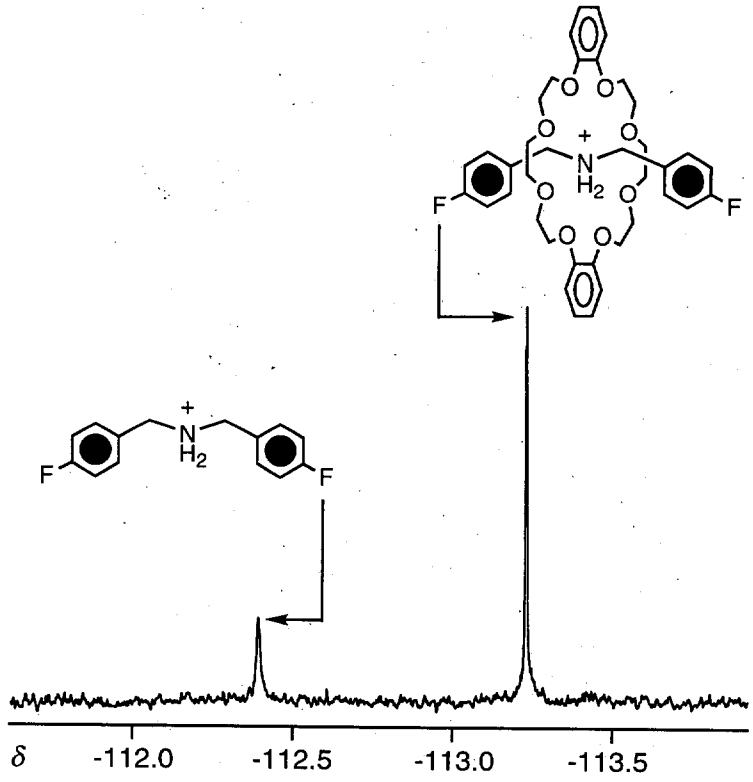


Figure S7. The partial ^{19}F NMR spectrum (376 MHz, 300 K) of a CD_3CN solution containing a 1:1 mixture of DB24C8 (**2**) and the *p*-F-substituted dibenzylammonium salt **14**-H·PF_6.

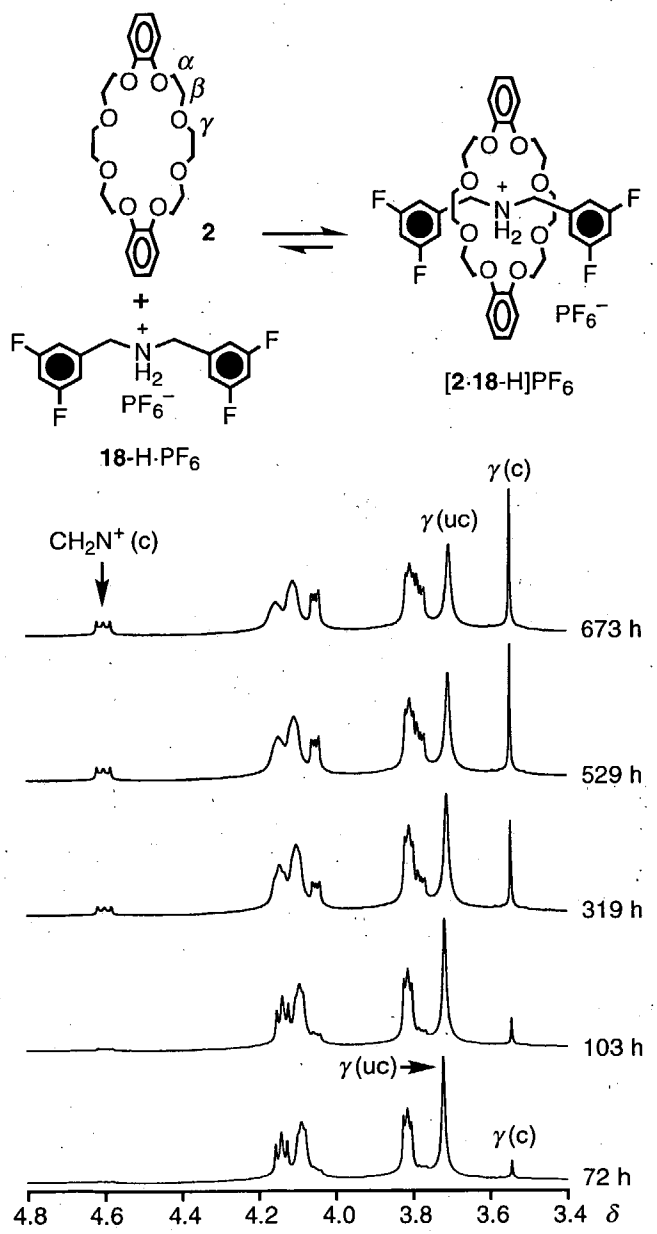


Figure S8. Partial ^{1}H NMR spectra (400 MHz, 300 K) recorded over time of a $CDCl_3/CD_3CN$ (3:1) solution containing a 1:1 mixture of DB24C8 (**2**) and the bis(3,5-difluoro)-substituted dibenzylammonium ion salt **18**-H·PF_6 in a sealed NMR tube.

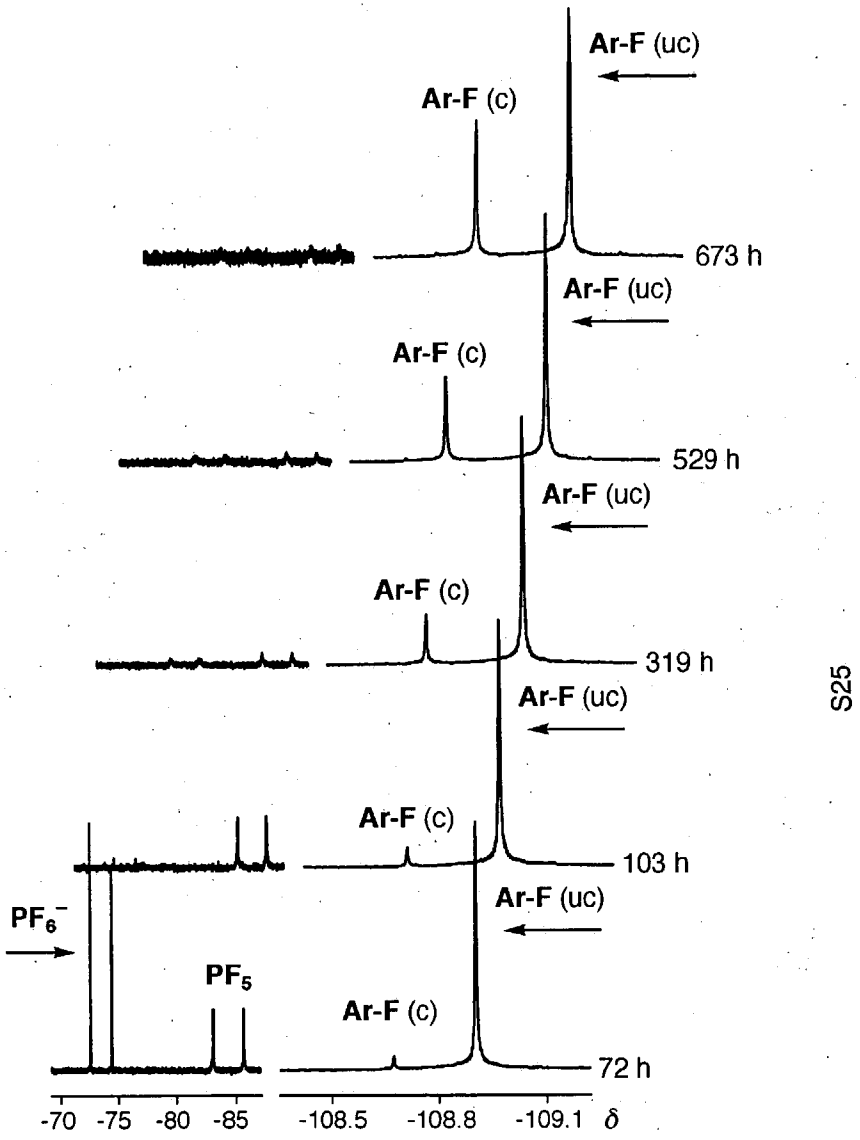


Figure S9. Partial ^{19}F NMR spectra (376 MHz, 300 K) recorded over time of a $CDCl_3/CD_3CN$ (3:1) solution containing a 1:1 mixture of DB24C8 (**2**) and the bis(3,5-difluoro)-substituted dibenzylammonium ion salt **18**-H·PF_6 in a sealed NMR tube, reveal that the PF_6^- anion decomposes in a matter of days under these conditions.

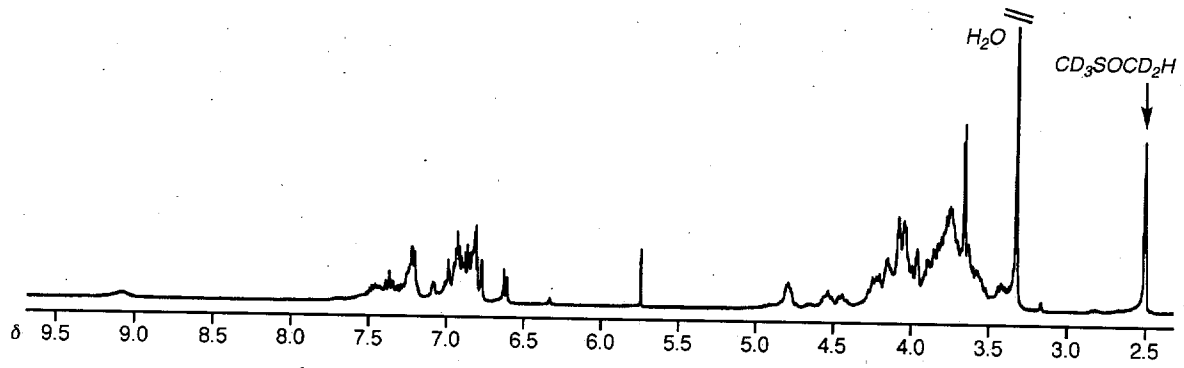


Figure S10. Surprisingly, the ^{1}H NMR spectrum (400 MHz, 300 K) of **21**-H·PF_6, obtained immediately after its dissolution in CD_3SOCD_3, indicated the presence of aggregated daisy chain superstructures.

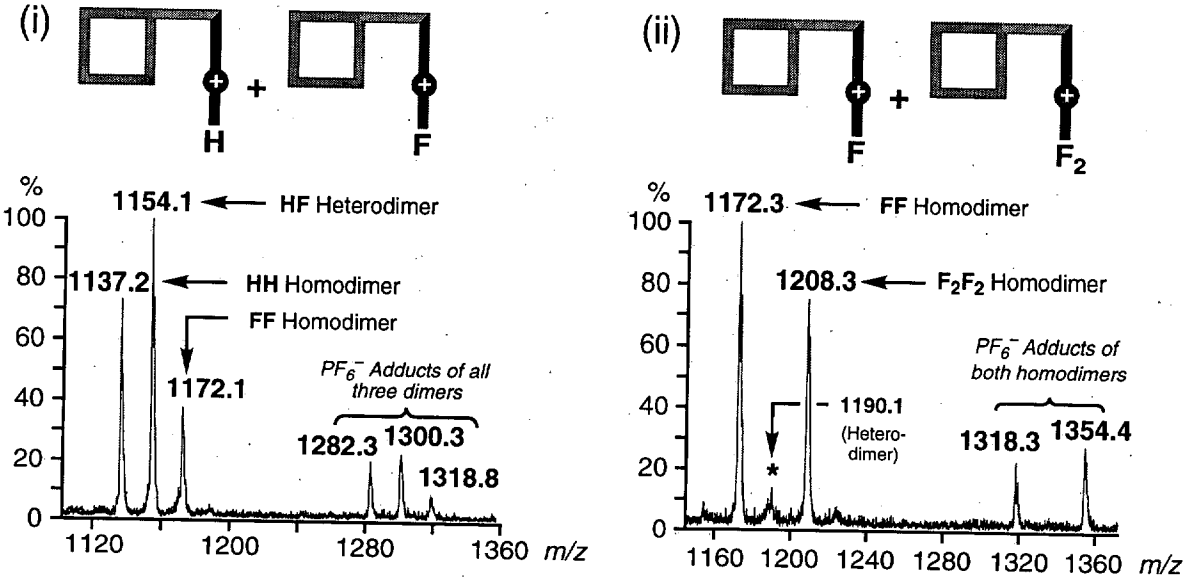


Figure S11. The FAB-mas spectra of **21**-H·PF_6 (i) prior to dissolution in CD_3SOCD_3, and (ii) after sitting in CD_3SOCD_3 solution for 6 d.

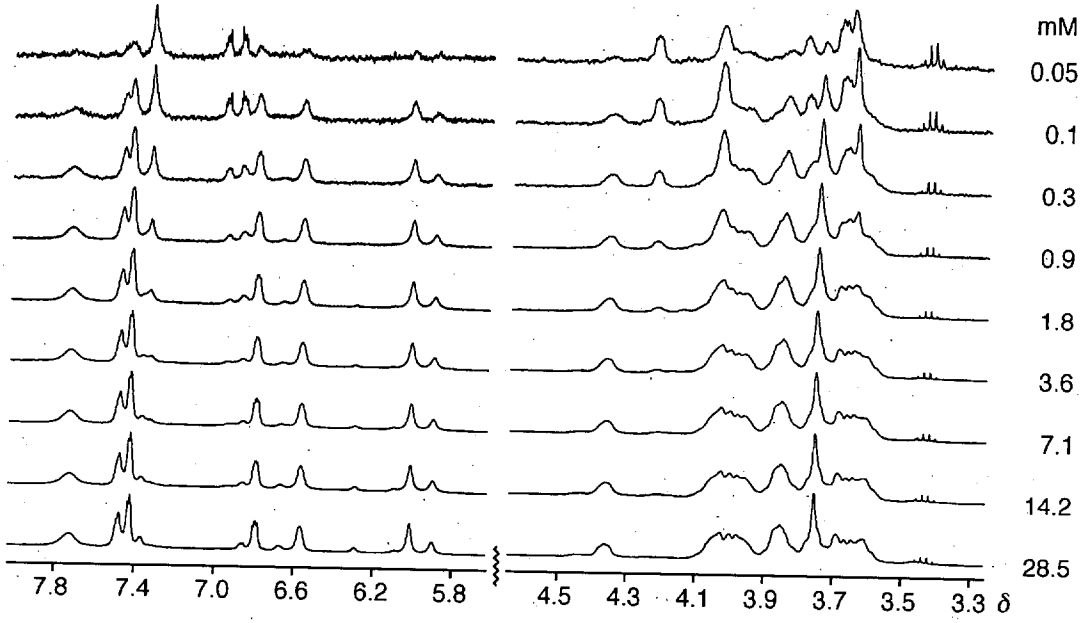


Figure S12. The concentration-dependent partial ^{1}H NMR spectra (400 MHz, 300 K) of CD_2Cl_2 solutions of the parent [25]crown-8 daisy chain monomer (**22**-H·PF_6).

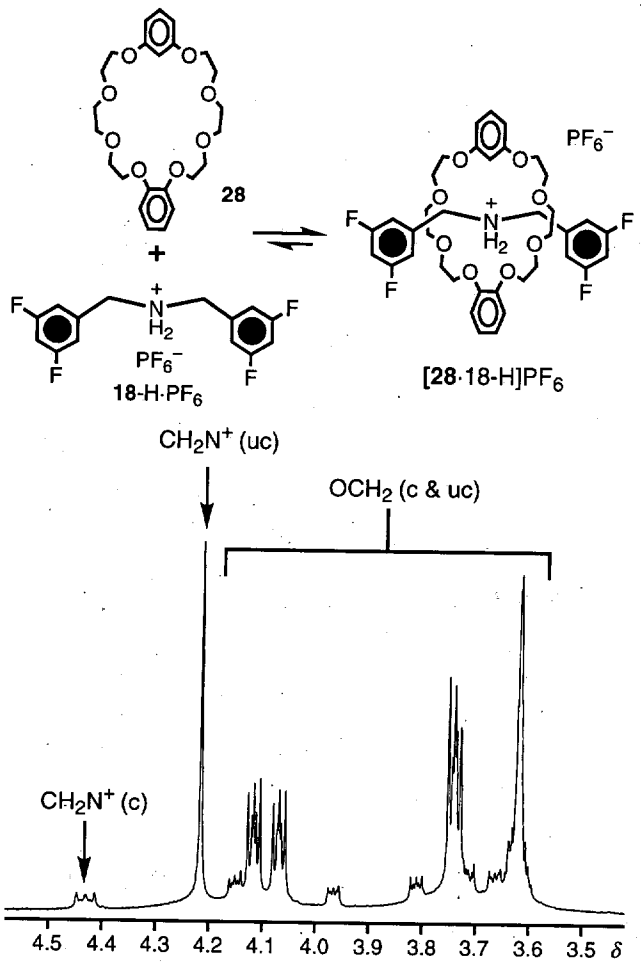


Figure S13. The partial ^{1}H NMR spectrum (400 MHz, 300 K) of a CD_3CN solution containing a 1:1 mixture of BMP25C8 (**28**) and the 3,5-difluorophenyl-substituted dibenzylammonium salt **18**-H·PF_6.

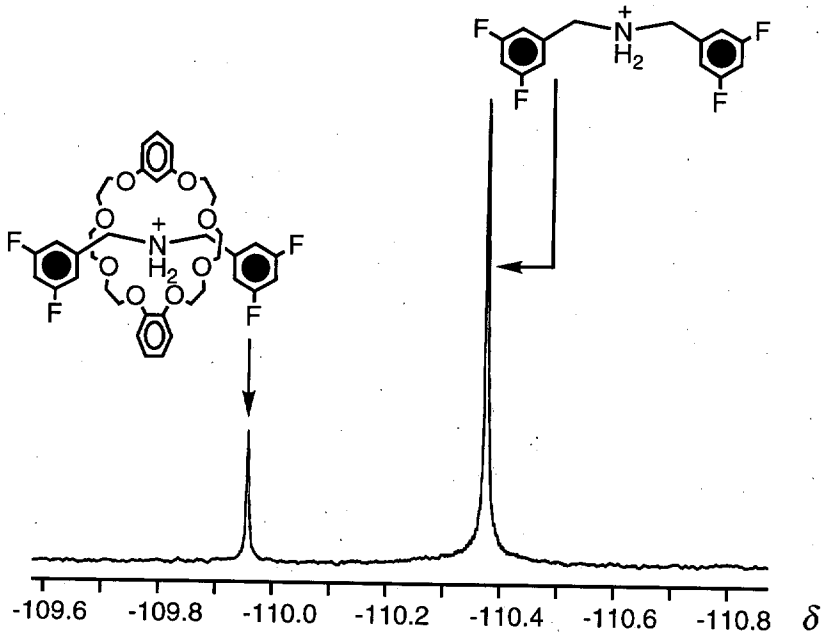
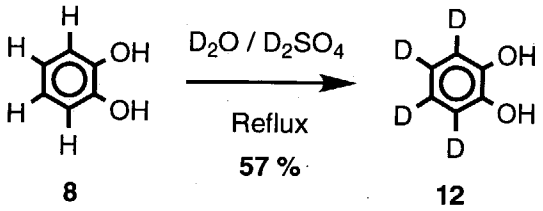
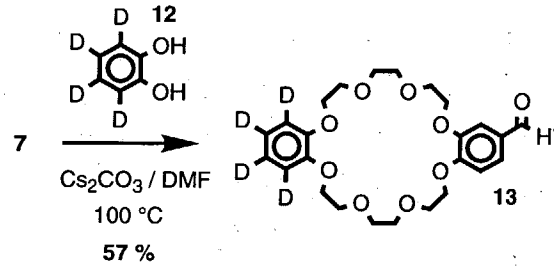


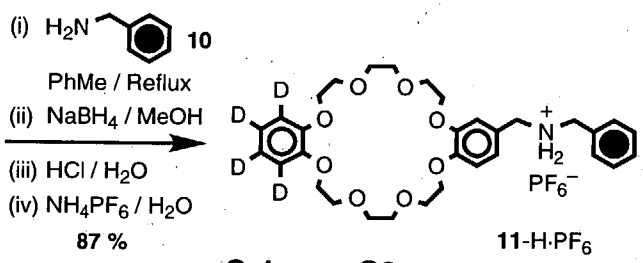
Figure S14. The partial ^{19}F NMR spectrum (376 MHz, 300 K) of a 1:1 mixture of BMP25C8 (**28**) and **18**-H·PF_6 reveals the presence of two aromatic F signals, one corresponding to free **18**-H·PF_6, and the other to the [2]pseudorotaxane [**28**·**18**-H]PF_6.



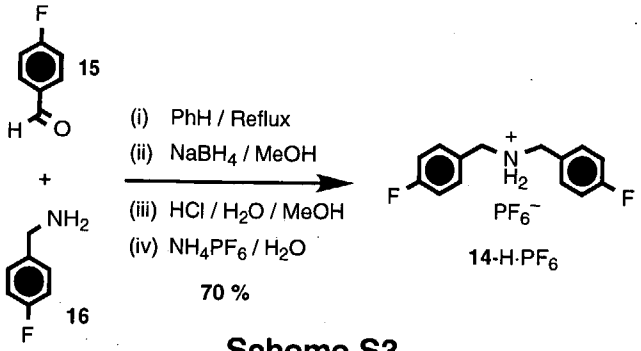
8 12

Scheme S1

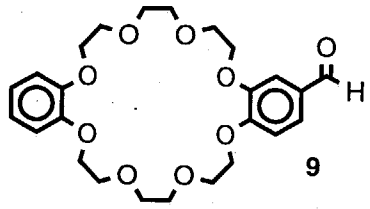


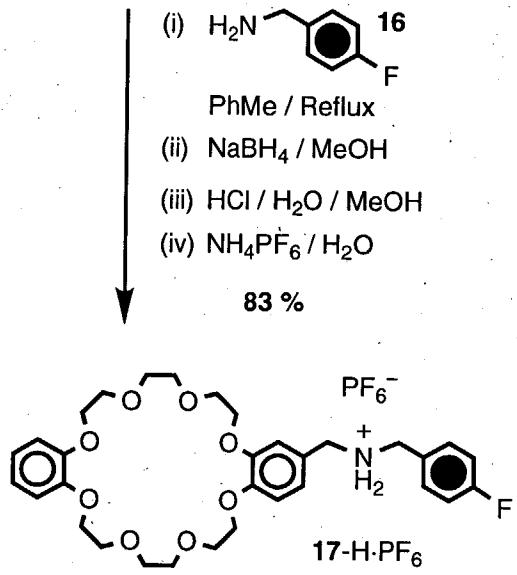


Scheme S2

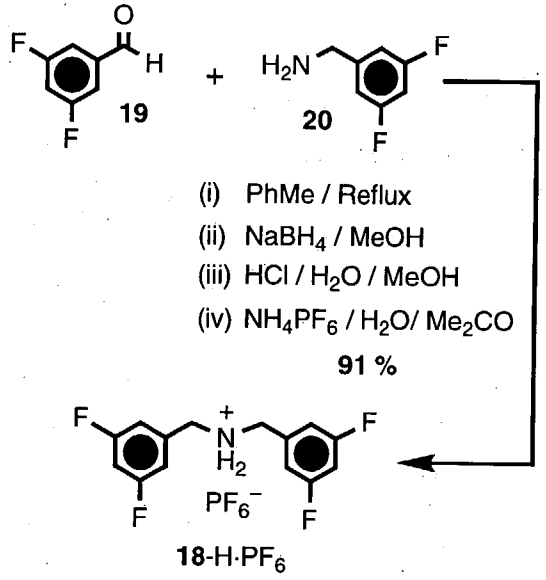


Scheme S3

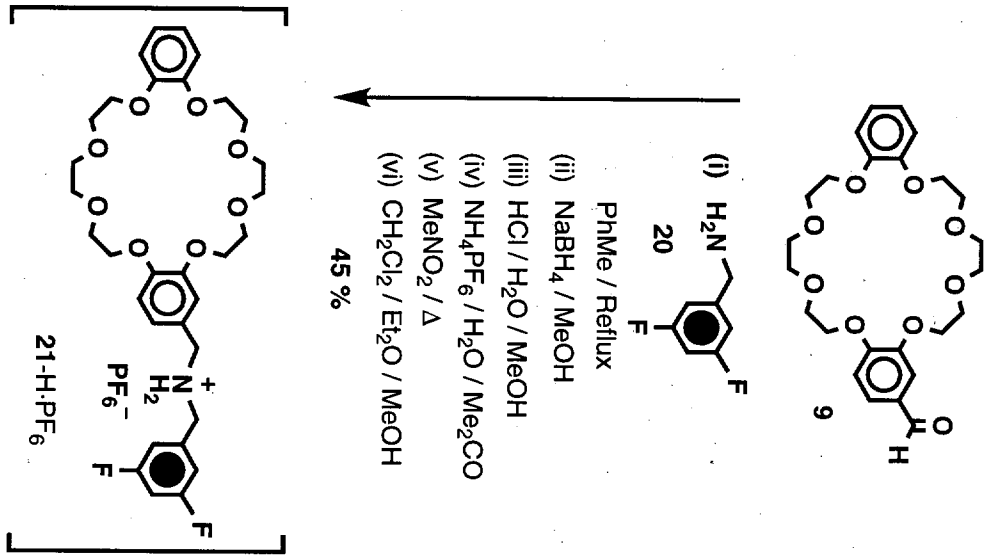




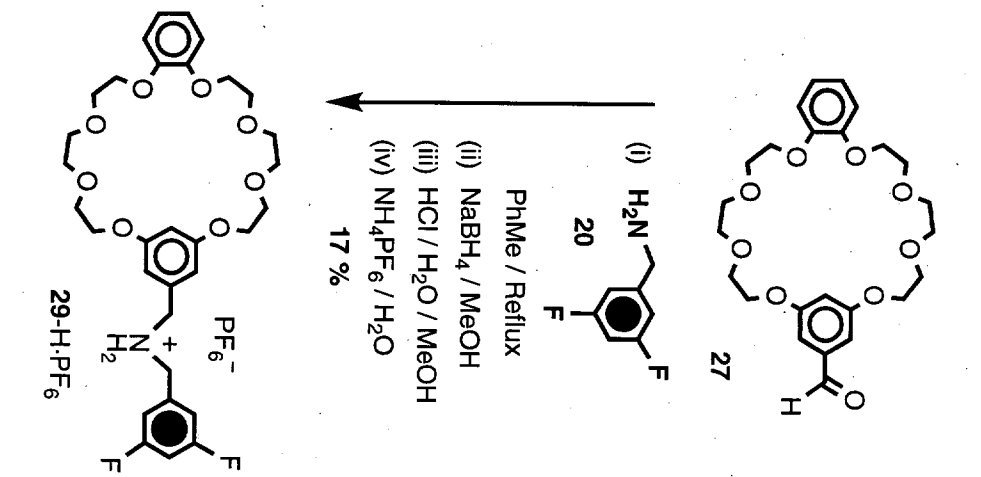
Scheme S4



Scheme S5



Scheme S6



Scheme S7

Experimental

(2-Formyl)dibenzo{catechol-d_4}[24]crown-8 (13). Cesium carbonate (46.5 g, 143 mmol) was placed in a 2 L round-bottomed flask fitted with condenser and pressure equalized dropping funnel. The system was flushed with N_2 and anhydrous DMF (500 mL) was added to the flask. The ditosylate **7** (8.43 g, 11.9 mmol) and d_4-catechol (**12**) (3.26 g, 28.6 mmol) were dissolved in DMF (1 L) and added to the dropping funnel, again through a flow of N_2. The suspension in the flask was heated to 100 °C whilst stirring, and the ditosylate/d_4-catechol solution was added dropwise over 48 h. This mixture was stirred at 100 °C—under an N_2 atmosphere—for a further 3 d. Upon cooling down, the reaction mixture was filtered, the solvent removed *in vacuo*, and the residue partitioned between PhMe (300 mL) and 10 % w/v K_2CO_3 solution (300 mL). The aqueous layer was further extracted with PhMe (4 x 300 mL) and the combined organic layers were washed with 10 % w/v K_2CO_3 solution (300 mL). The organic phase was dried ($MgSO_4$) and the solvents removed *in vacuo*. The residue was subjected to column chromatography (SiO_2 : gradient elution with EtOAc/MeOH, 100:0 to 96:4) to yield a white solid which was recrystallized from EtOAc/C_6H_{14} to yield the desired compound **13** as a white solid (7.79 g, 57 %); m.p. 108–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81–3.85 (m, 8H), 3.89–3.96 (m, 8H), 4.11–4.22 (m, 8H), 6.92 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 2.0 Hz, 1H), 7.40 (dd, J = 2.0, 8.0 Hz, 1H), 9.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 69.4, 69.5, 69.6, 69.7, 69.8, 70.0, 71.4, 71.5, 71.6, 111.1, 112.0, 113.1–114.0 (^{2}H-coupled multiplet), 120.6–121.4 (^{2}H-coupled multiplet), 126.9, 130.3, 148.9, 149.3, 139.8, 154.4, 191.0; MS (FAB): *m/z* (%): 481.4 (100) $[M+H]^+$; HRMS (FAB): calcd for $[M]^+$ ($C_{25}H_{28}D_4O_9$) 480.2297, found 480.2319; $C_{25}H_{28}D_4O_9$ (480.5): calcd C 62.49, H+D 7.55; found C 62.61, "H" 6.83. Note: Combustion analysis does not discriminate between H_2O, HOD, and D_2O, therefore, the theoretical values (%) for C and H will not be observed in the analysis of a pure sample of this compound. After combustion, all water vapor detected (on a thermal conductivity, *not* a mass, basis) passing through the GC column is assumed to be H_2O (rather than other, heavier, isotopic forms), and, as such, a correct composition analysis will reflect the C and H values (%) for the undeuterated analogue of the compound. In this case, the observed values (*vide supra*) are within 0.4 % of those expected (C 63.01, H 6.77) for the unlabeled analogue.

(2-Benzylammoniummethyl)dibenzo{catechol-d_4}[24]crown-8 Hexafluorophosphate (11-H·PF_6). Conversion of **13** (761 mg, 1.58 mmol) into the corresponding d_4-daisy chain monomer **11-**

H·PF_6 was achieved using the same procedures as described previously for the non-deuterated analogue. The target compound (**11**-H·PF_6) was obtained as a white solid (280 mg, 87 % over three steps); m.p. 208–211 °C (decomp.); ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 3.64–3.68 (m, 8H), 3.74–3.81 (m, 8H), 4.03–4.14 (m, 12H), 6.97–7.03 (m, 2H), 7.36 (s, 1H), 7.39–7.51 (m, 5H); ^{13}C NMR (125 MHz, CD_3SOCD_3): δ = 50.2, 50.3, 69.0, 69.1, 69.2, 69.4, 69.5, 70.7, 70.8, 113.5–114.3 (^{2}H-coupled multiplet) overlapping with a singlet at 113.8, 115.8, 120.6–121.3 (^{2}H-coupled multiplet), 123.4, 124.4, 129.1, 129.4, 130.3, 132.2, 148.5, 148.7, 149.3; MS (FAB): *m/z* (%): 572.3 (87) $[M–PF_6]^+$ and $[2M–2PF_6]^{2+}$, 1143.6 (100) $[2M–H–2PF_6]^+$, 1289.8 (37) $[2M–PF_6]^+$; HRMS (FAB): calcd for $[M–PF_6]^+$ ($C_{32}H_{38}D_4NO_8$) 572.3158, found 572.3157; $C_{32}H_{42}NO_8PF_6·0.5H_2O$ (721.1): calcd C 53.19, H 6.00, N 1.94; found C 53.10, H 5.94, N 1.88. Note: As with **13**, the composition analysis assumes the compound to contain only protium, and no deuterium.

Bis(4-fluorobenzyl)ammonium Hexafluorophosphate (**14**-H·PF_6). A solution of 4-fluorobenzylamine (**16**) (5.00 g, 40.0 mmol) and 4-fluorobenzaldehyde (**15**) (4.96 g, 40.0 mmol) in C_6H_6 (150 mL) was heated under reflux for 20 h using a Dean-Stark apparatus. The resulting solution was evaporated to dryness, the residue dissolved in dry MeOH (100 mL), and $NaBH_4$ (7.57 g, 200 mmol) was added portionwise over a period of 10 min. After stirring under ambient conditions for 4 h, the reaction mixture was quenched with an excess of 12M HCl solution. The solvents were removed *in vacuo*, and the residue was partitioned between NaOH solution (5N, 250 mL) and CH_2Cl_2 (250 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 250 mL), the combined organic extracts were dried ($MgSO_4$), and the resulting solution was evaporated to dryness to yield a colorless oil. The oil was subsequently dissolved in MeOH (200 mL) and 12M HCl solution (25 mL) was added carefully. After stirring for *ca.* 10 min, the solvents were removed *in vacuo* to give a white solid, which was then dissolved in hot H_2O. A minor amount of insoluble material was removed by hot filtration, and addition of an excess of saturated aqueous NH_4PF_6 to this solution resulted in the precipitation of the desired compound, which was collected and dried to give a white solid (10.6 g, 70 %); m.p. 229–231 °C (decomp.); ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 4.23 (s, 4H), 6.99 (br s, 2H), 7.16–7.23 (m, 4H), 7.48–7.54 (m, 4H); ^{19}F NMR (376 MHz, CD_3SOCD_3): δ = –71.9 (d, J = 706 Hz, 6F), –112.4 (s, 2F); ^{13}C NMR (100 MHz, CD_3SOCD_3): δ = 51.5, 116.7 (d, J = 21.8 Hz), 127.3 (d, J = 3.3 Hz), 133.5 (d, J = 8.7 Hz), 164.2 (d, J = 245 Hz); MS (FAB): *m/z* (%): 234.2 (100) $[M–PF_6]^+$; HRMS (FAB): calcd for $[M–PF_6]^+$ ($C_{14}H_{14}NF_2$) 234.1095, found 234.1098; $C_{14}H_{14}NPF_8·0.75H_2O$ (392.7): calcd C 42.81, H 3.98, N 3.57; found C 42.56, H 3.54, N 3.38.

(2-[4-Fluorobenzyl]ammoniummethyl)dibenzo[24]crown-8 Hexafluorophosphate (**17**·H·PF_6). A solution of the formyl-substituted crown ether **9** (750 mg, 1.57 mmol) and 4-fluorobenzylamine (**16**) (197 mg, 1.57 mmol) in PhMe (100 mL) was heated under reflux for 16 h using a Dean-Stark apparatus. The resulting solution was evaporated to dryness, the residue dissolved in dry MeOH (75 mL), and $NaBH_4$ (605 mg, 16.0 mmol) was added portionwise over a period of 10 min. After stirring under ambient conditions for 40 h, the reaction mixture was quenched with an excess of 12M HCl solution. The solvents were removed *in vacuo*, and the residue was partitioned between NaOH solution (5N, 250 mL) and CH_2Cl_2 (250 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 250 mL), the combined organic extracts were dried ($MgSO_4$), and the resulting solution was evaporated to dryness to yield a colorless oil. The oil was subsequently dissolved in MeOH (50 mL) and 12M HCl solution (5 mL) was added carefully. After stirring for *ca.* 10 min, the solvents were removed *in vacuo* to give an oil, which was then dissolved in hot H_2O. A minor amount of insoluble material was removed by hot filtration, and addition of an excess of saturated aqueous NH_4PF_6 to this solution resulted in the precipitation of a white solid. Upon collection, the solid was washed with copious amounts of H_2O, and finally Et_2O to afford the desired compound as a powdery white solid (972 mg, 83 %); m.p. 195–199 °C (decomp.); ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 3.65–3.68 (m, 8H), 3.74–3.81 (m, 8H), 4.04–4.14 (m, 12H), 6.85–6.96 (m, 4H), 7.00 (s, 2H), 7.12 (s, 1H), 7.25–7.32 (m, 2H), 7.50–7.57 (m, 2H), 9.09 (br s, 2H); ^{19}F NMR (376 MHz, CD_3SOCD_3): δ = –69.7 (d, J = 711 Hz, 6F), –112.3 (s, 1F); ^{13}C NMR (125 MHz, CD_3SOCD_3): δ = 49.1, 49.9, 68.7, 68.8, 68.9, 69.4, 69.1, 69.2, 70.4, 70.5, 113.5, 114.1 (d, J = 3.7 Hz), 115.5, 115.7, 121.2, 123.0, 124.2, 128.3 (d, J = 3.1 Hz), 132.4 (d, J = 8.5 Hz), 148.3, 148.5, 149.0, 162.4 (d, J = 244 Hz); MS (FAB): *m/z* (%): 586.5 (90) $[M–PF_6]^+$ and $[2M–2PF_6]^{2+}$, 1172.0 (100) $[2M–H–2PF_6]^+$, 1318.1 (15) $[2M–PF_6]^+$; $C_{32}H_{41}NO_8PF_7$ (731.6): calcd C 52.53, H 5.65, N 1.91; found C 52.55, H 5.43, N 1.69.

Bis(3,5-difluorobenzyl)ammonium Hexafluorophosphate (**18**·H·PF_6). A solution of 3,5-difluorobenzylamine (**20**) (1.01 g, 7.06 mmol) and 3,5-difluorobenzaldehyde (**19**) (1.00 g, 7.04 mmol) in PhMe (100 mL) was heated under reflux for 20 h using a Dean-Stark apparatus. The resulting solution was evaporated to dryness, the residue dissolved in dry MeOH (75 mL), and $NaBH_4$ (2.65 g, 70.1 mmol) was added portionwise over a period of 10 min. After stirring under ambient conditions for 40 h, the reaction mixture was quenched with an excess (~5 mL) of 12M HCl solution. The solvents were removed *in vacuo*, and the residue was partitioned between NaOH solution (2N,

250 mL) and CH_2Cl_2 (250 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 250 mL), the combined organic extracts were dried ($MgSO_4$), and the resulting solution was evaporated to dryness to yield a colorless oil. The oil was subsequently dissolved in MeOH (200 mL) and 12M HCl solution (5 mL) was added carefully. After stirring for *ca.* 10 min, the solvents were removed *in vacuo* to give a white solid, which was washed with Et_2O. This solid was dissolved in a 1:1 mixture of Me_2CO/H_2O (400 mL) and an excess (~ 2.0 g) of solid NH_4PF_6 was added to this solution. Whilst this solution was being concentrated under reduced pressure to a volume of *ca.* 200 mL a white precipitate appeared. Subsequent addition of H_2O (300 mL) resulted in more precipitation. After collection and drying, the desired product was obtained as a white solid (2.64 g, 91 %); m.p. 231–233 °C; ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 4.27 (s, 4H), 7.02–7.20 (m, 8H); ^{19}F NMR (376 MHz, CD_3SOCD_3): δ = –71.7 (d, J = 706 Hz, 6F), –109.1 (s, 4F); ^{13}C NMR (100 MHz, CD_3SOCD_3): δ = 51.2, 106.1 (t, J = 25.5 Hz), 114.1–114.4 (m), 134.6 (t, J = 9.8 Hz), 163.8 (dd, J = 12.9, 247 Hz); MS (FAB): *m/z* (%): 270.2 (100) $[M–PF_6]^+$; HRMS (FAB): calcd for $[M–PF_6]^+$ ($C_{14}H_{12}NF_4$) 270.0906, found 270.0902; $C_{14}H_{12}NPF_{10}$ (415.2): calcd C 40.50, H 2.91, N 3.37; found C 40.55, H 2.79, N 3.26.

(2-[3,5-Difluorobenzyl]ammoniummethyl)dibenzo[24]crown-8 Hexafluorophosphate (21-H·PF_6). A solution of the formyl-substituted crown ether **9** (750 mg, 1.57 mmol) and 3,5-difluorobenzylamine (**20**) (225 mg, 1.57 mmol) in PhMe (150 mL) was heated under reflux for 20 h using a Dean-Stark apparatus. The resulting solution was evaporated to dryness, the residue dissolved in dry MeOH (75 mL), and $NaBH_4$ (605 mg, 16.0 mmol) was added portionwise over a period of 5 min. After stirring under ambient conditions for 40 h, the reaction mixture was quenched with an excess (~5 mL) of 12M HCl solution. The solvents were removed *in vacuo*, and the residue was partitioned between NaOH solution (2N, 250 mL) and CH_2Cl_2 (250 mL). The aqueous layer was further extracted with CH_2Cl_2 (3 x 250 mL), the combined organic extracts were dried ($MgSO_4$), and the resulting solution was evaporated to dryness to yield a colorless oil. The oil was subsequently dissolved in MeOH (50 mL) and 12M HCl solution (5 mL) was added carefully. After stirring for *ca.* 10 min, the solvents were removed *in vacuo* to give an oil, which was then dissolved in a 1:1 mixture of Me_2CO/H_2O (400 mL) and an excess (~ 2.0 g) of solid NH_4PF_6 was added to this solution. The solution was concentrated under reduced pressure—until no Me_2CO remained—and the oily H_2O-insoluble residue was extracted into CH_3NO_2 (3 x 50 mL). After drying ($MgSO_4$), the solvent was removed *in vacuo* to afford a sticky semi-solid residue, which was dissolved in CH_2Cl_2 (100 mL). A small amount of CH_2Cl_2-insoluble material was recovered, and determined to be NH_4PF_6. Addition

of Et_2O (~100 mL) to the CH_2Cl_2 solution resulted in the precipitation of a sticky solid, which was redissolved upon addition of a small amount of MeOH (~ 10 mL). On leaving this solution to stand, a white solid *slowly* precipitated from solution over the course of the next month, which was collected by filtration and dried. Further treatment of the mother liquor with (i) Et_2O, and (ii) MeOH, caused further slow precipitation. In total, three crops of white solid were collected (535 mg, 45 %); m.p. 213–215 °C. The following NMR spectroscopic data is for the monomeric species, **21**-H·PF_6, after the isolated material was allowed to de-thread in CD_3SOCD_3 over a period of 7 d. ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 3.65–3.68 (m, 8H), 3.73–3.81 (m, 8H), 4.04–4.12 (m, 10H), 4.19 (s, 2H), 6.84–6.90 (m, 2H), 6.92–6.96 (m, 2H), 6.98–7.04 (m, 2H), 7.10 (d, J = 1.2 Hz, 1H), 7.22–7.29 (m, 2H), 7.34 (tt, J_{HH} = 2.0 Hz, J_{HF} = 9.6 Hz, 1H), 9.11 (br s, 2H); ^{19}F NMR (376 MHz, CD_3SOCD_3): δ = –69.7 (d, J = 711 Hz, 6F), –108.8 (s, 2F); ^{13}C NMR (100 MHz, CD_3SOCD_3): δ = 48.8, 50.2, 68.7, 68.8, 68.9, 69.1, 69.2, 70.4, 70.5, 104.5 (t, J = 25.5 Hz), 113.1–113.4 (m), 114.0, 114.1, 115.5, 121.2, 123.1, 124.0, 136.0 (t, J = 9.9 Hz), 148.2, 148.5, 149.1, 162.2 (dd, J = 13.2, 245 Hz); MS (FAB): *m/z* (%): (i) of isolated material; 604.4 (100) [M–PF_6]$^+$ and [2M–2PF_6]$^{2+}$, 1207.9 (77) [2M–H–2PF_6]$^+$, 1318.1 (31) [2M–PF_6]$^+$; (ii) of material after DMSO-induced dethreading; 604.3 [M–PF_6]$^+$ *only*; $C_{32}H_{40}NO_8PF_8$ (749.6): calcd C 51.27, H 5.38, N 1.87; found C 51.22, H 5.37, N 1.80.

(5-[{3,5-Difluorobenzyl}ammoniummethyl]metaphenylene)[25]crown-8 Hexafluorophosphate (**29**-H·PF_6). A solution of the formyl-substituted crown ether **27** (498 mg, 1.05 mmol) and 3,5-difluorobenzylamine (**20**) (150 mg, 1.05 mmol) in PhMe (50 mL) was heated under reflux for 24 h using a Dean-Stark apparatus. The resulting solution was evaporated to dryness, the residue dissolved in dry MeOH (100 mL), and $NaBH_4$ (198 mg, 5.23 mmol) was added portionwise over a period of 5 min. After stirring under ambient conditions for 24 h, the reaction mixture was evaporated to dryness, and the residue was partitioned between NaOH solution (2N, 200 mL) and CH_2Cl_2 (200 mL). The aqueous layer was further extracted with CH_2Cl_2 (2 x 250 mL), the combined organic extracts were dried ($MgSO_4$), and the resulting solution was evaporated to dryness to yield a colorless oil. This oil was subsequently dissolved in MeOH (100 mL) and 12M HCl solution (10 mL) was added carefully. After stirring for *ca.* 10 min, the solvents were removed *in vacuo* and the residue dissolved in hot H_2O. Addition of an excess of saturated aqueous NH_4PF_6 to this solution resulted in the precipitation of a white solid. Upon collection, the solid was dissolved in CH_2Cl_2, and precipitated with Et_2O to afford the desired compound as a powdery white solid (143 mg, 18 %); m.p.

180–182 °C (decomp.); ^{1}H NMR (400 MHz, CD_3SOCD_3): δ = 3.57–3.62 (m, 8H), 3.69–3.75 (m, 8H), 4.03–4.09 (m, 6H), 4.13–4.17 (m, 4H), 4.20 (s, 2H), 6.65 (d, J = 2.0 Hz, 2H), 6.72 (t, J = 2.0 Hz, 1H), 6.84–6.89 (m, 2H), 6.92–6.98 (m, 2H), 7.21–7.28 (m, 2H), 7.34 (tt, J_{HH} = 2.4 Hz, J_{HF} = 9.6 Hz, 1H), 9.14 (br s, 2H); ^{19}F NMR (376 MHz, CD_3SOCD_3): δ = –69.7 (d, J = 711 Hz, 6F), –108.8 (s, 2F); ^{13}C NMR (100 MHz, CD_3SOCD_3): δ = 49.1, 50.3, 67.7, 68.1, 69.1, 70.1, 70.2, 102.3, 104.6 (t, J = 25.2 Hz), 108.9, 113.2–113.4 (m), 114.3, 121.2, 133.6, 135.9 (t, J = 9.9 Hz), 148.3, 159.9, 162.2 (dd, J = 13.2, 245 Hz); MS (FAB): *m/z* (%): 604.4 (100) $[M–PF_6]^+$ and $[2M–2PF_6]^{2+}$, 1207.8 (76) $[2M–H–2PF_6]^+$, 1353.9 (8) $[2M–PF_6]^+$; $C_{32}H_{40}NO_8PF_8$ (749.6): calcd C 51.27, H 5.38, N 1.87; found C 51.10, H 5.43, N 1.85.